Spring 2017

HYDROLOGIC AND CHEMICAL INTERACTION BETWEEN WASTE DUMPS AND A FLOODED MINE POOL AT THE COMBINATION MINE, PHILIPSBURG DISTRICT, MONTANA

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by

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A thesis submitted in partial fulfillment of the
requirements for the degree of

Masters of Science in Geoscience:
Hydrogeological Engineering Option

Montana Tech

2017

Abstract

The Combination Mine, located approximately 12 miles northwest of Philipsburg Montana, was intermittently mined for silver, gold, and copper from 1885 until the 1990s. After the Combination Mine was formally abandoned groundwater seeps downgradient of the mine and waste rock pile were found to be above the regulatory water quality standards. Since the groundwater seeps were downgradient of both the mine pool and waste rock pile the source of the groundwater seeps could have been from the mine pool or shallow flow paths through the waste rock pile. In order to properly plan and execute a remedial action on the groundwater seeps it was important to determine the source of their recharge.

This study investigated the source of recharge to several groundwater seeps in the Combination Mine vicinity. Stable water isotopes (δ^2H, $\delta^{18}O$) were used to identify potential pathways of recharge to the groundwater seeps. Temporal changes in geochemistry were monitored to identify dilution and differences in hydraulic residence time. Sulfate isotope ($\delta^{34}S$ and $\delta^{18}O$) samples were collected and analyzed to determine if different recharge sources could be identifed. Benchtop experiments were done in which 2 kg samples of mine waste were interacted with water for a week, with the leachate samples analyzed for pH, metal concentration, and $\delta^{18}O$ and $\delta^{34}S$ of dissolved sulfate. Through the use of these methods it was determined that for the largest groundwater discharge is likely influenced by the mine pool. However other small seeps appeared to be less likely to be influenced by the mine pool water.

Keywords: Stable isotopes, Sulfate isotopes, groundwater seeps, abandon mine

Acknowledgements

Without the incredible patience of Dr. Chris Gammons this thesis would have never been finished. I would also like to thank Devin Clary and the Montana Department of Environmental Quality for providing funding for isotopic analysis. I am very grateful to the Geological Engineering department at Montana Tech for their generous support and valuable mentoring. Blane Dale and Herrera Environmental Consultants along with Luke Darnell and Trihydro Corporation were extremely helpful in sharing historic and current data of the site and letting me piggyback on their sampling to collect additional sample volumes. I also owe a huge thank you to Gary Wyss who helped me running samples on the ICP-OES, along with my fellow grad students Heather Boese and Seth Reedy who helped me numerous times throughout this process.

Committee members, Drs. Glenn Shaw and Raja Nagisetty

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Glossary of Terms

Term	Definition
As	Arsenic
ASARCO	American Smelting and Refining Company
B.D.	Below detection limits
Cd	Cadmium
Cu	Copper
Fe	Iron
gpm	Gallons per minute
H	Hydrogen
HCl	Hydrochloric acid
HDPE	High-density polyethylene
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
Kg	Kilograms
LEL	Local evaporation line
MDEQ-AML	Montana Department of Environmental Quality Abandon Mine Lands Bureau
mg/L	Milligrams per liter
mL	Milliliters
Mn	Manganese
MWL	Meteoric water line
O	Oxygen
Pb	Lead
PES	Polyethersulfone
S	Sulfur
Sb	Antimony
SC	Specific conductance
µS/cm	MicroSiemens per centimeter

1. Introduction

Montana has a long history of mining and when the valuable minerals are exhausted these mines are closed and abandoned. Currently there are approximately 4,915 abandoned mines in Montana (Bureau of Land Management, 2007). The environmental impacts of these mines can last long after the mine has been closed. If proper remediation activities are not completed the abandoned mine can lead to degradation of both ground water and surface water quality. Once an underground mine is closed the groundwater level is often allowed to return to the pre-mining level and flood the underground mine workings. Along with the flooded mine pool, waste rock piles are often found near the mine. Flooded mine pool water and runoff from tailings/waste rock piles can result in decreased water pH and high metal loadings in the groundwater and surrounding surface water.

Groundwater seeps expressing themselves in a mine-impacted area are one potential source of low pH and high metal concentration water into local streams. Identifying the source of water to these seeps, whether it is from the flooded mine pool or shallow flow paths through the waste rock, is imperative to successful remediation. The use of stable isotopes is one method to help identify the source of water to groundwater seeps. Stable water isotopes (δ^2H, $\delta^{18}O$) have been used in the past to determine the origin of water in mining areas (Hazen et al., 2002; Walton-Day & Poeter, 2009; Gammons et al., 2013a). Researchers have used $\delta^{34}S$ and $\delta^{18}O$ of sulfate to identify the source of dissolved sulfate in mine-impacted water (Toran, 1987; Otero & Soler, 2002; Edraki et al., 2005; Gammons et al., 2013b)

Stable water isotopes are conservative in aquifers over relatively short periods of time but on the surface can change due to evaporation (Clark and Fritz, 1997). Meteoric stable water isotopes usually fall close to the global metoric water line $\delta D = \delta^{18}O + 10$ (Craig, 1961). Where the

isotopes plot along the global metoric water line is affected by seasonal changes in weather.This seasonal change is a result of isotopically heavier water containing δ^2H and $\delta^{18}O$ preferentially remaining in liquid form (Aragus-Araguas et al., 2000). Due to the large seasonal changes of δ^2H and $\delta^{18}O$ in precipitation and the relative lack of seasonal changes of δ^2H and $\delta^{18}O$ in large groundwater reservoirs with long average residence time it is possible to identify the origins of seeps (Ghomshei & Allen, 2000).The use of sulfate as a hydrogeological tracer is beneficial since both $\delta^{18}O$ and $\delta^{34}S$ isotopes can be measured allowing the identification of the source of sulfate to the water (Seal 2003; Gammons et al., 2013b). The oxidation of sulfide minerals in an abandoned mine is a source of sulfate in water. When a sulfide mineral is oxidized, the S-isotope composition of dissolved sulfate that is formed is similar to the S-isotope composition of the starting sulfide (Seal, 2003). However, bacterial sulfate reduction may occur if conditions are anaerobic, leading to a shift in $\delta^{34}S$ of sulfate to more positive values (Canfield, 2001). The O-isotope composition of SO_4 depends on whether sulfide mineral oxidation is aerobic or anaerobic (Balci et al., 2007). Thus, measuring S- and O-isotopes of dissolved sulfate can be used as both a tracer of sources and a tracer of the geochemical environment that the sulfate molecule has seen.

1.1. Site Description

The Combination Mine (Figure 1) is part of the larger Black Pine mine complex which is located approximately 12 miles northwest of Philipsburg Montana. The Black Pine Mine property encompasses 1,055 acres of patented mining claims and an additional 157 unpatented claims located on United States Forest Service land (MDEQ-AML, 2012). In addition to the Combination Mine, the Black Pine Mine site also contains the Tim Smith Mine, the Historic Mine, and the Combination Mill (Figure 2). The Combination Mine is located at 6,500 feet

above sea level on a ridge between Smart Creek and Lower Willow Creek. The main and auxiliary adits for the Combination Mine are located on the east side of the ridge.

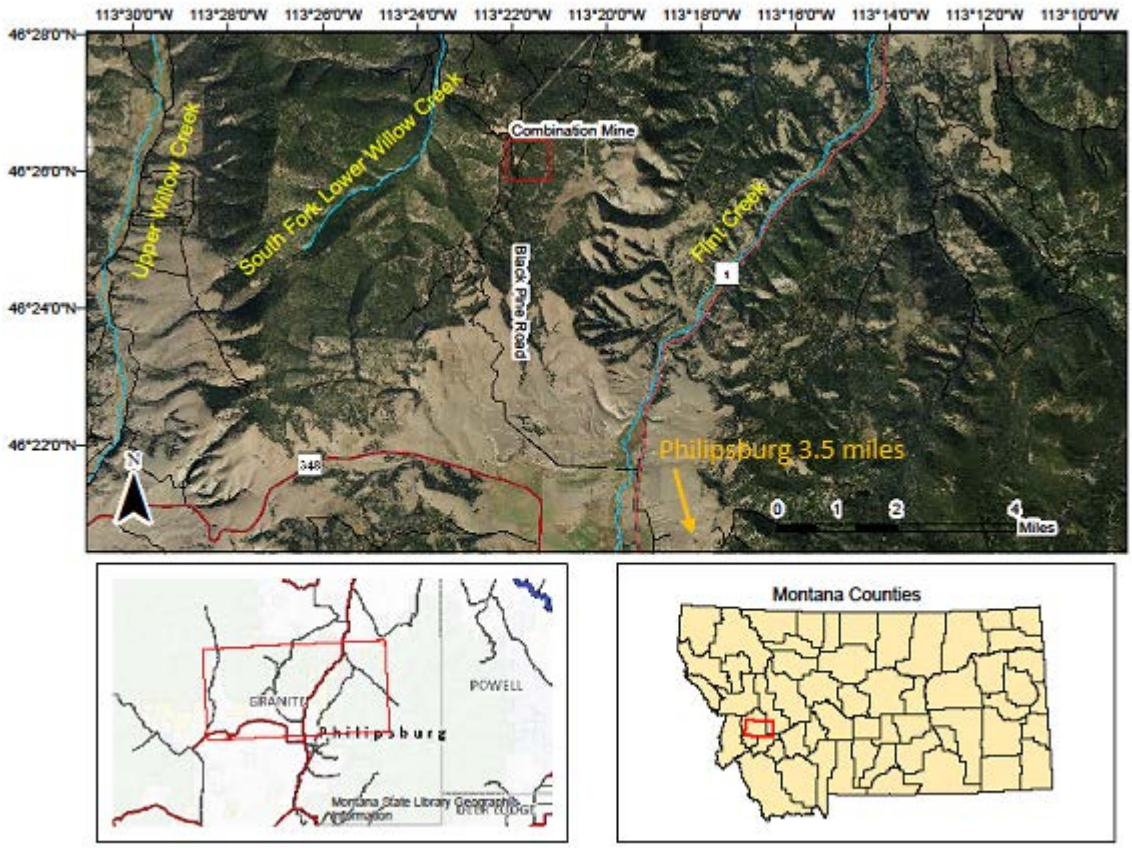

Figure 1: Map of Combination Mine location

The Mine was discovered in 1882 but mining activities did not begin until 1885 (Emmons & Calkins, 1913). The mine operated intermittently until the 1990s producing 5,622,000 ounces of silver, 3,000 ounces of gold, and 10,678,000 pounds of copper (Spanski, 2004). The last operator of the mine, American Smelting and Refining Company (ASARCO), mined silica ore in the Combination Mine to use as silica flux for their smelter in East Helena Montana. In 2005, ASARCO filed for bankruptcy resulting in the Montana Environmental Custodial trust taking

over the title to the Black Pine Mine site. The Montana Department of Environmental Quality Abandoned Mine Lands Bureau (MDEQ-AML) is the lead agency in remediation for the Black Pine Mine site. MDEQ-AML has contracted with Herrera Environmental and Trihydro Corporation to conduct remediation activities at the Black Pine Mine.

The Combination Mine is located in Member 2 of the Mount Shields Formation of the Mesoproterozoic Belt Supergroup (Figure 2). The Mount Shields formation is characterized by pink to gray quartzite (Lonn et al., 2003). Quartzite found at the Combination Mine is either reddish-brown or gray with well-rounded and closely packed grains. In the vicinity of the Black Pine Mine, the Mt. Shields Formation strikes N 30° W with a dip between 10°-20° to the west (Emmons & Calkins, 1913). There are numerous normal faults in the area with many of them striking ESE.

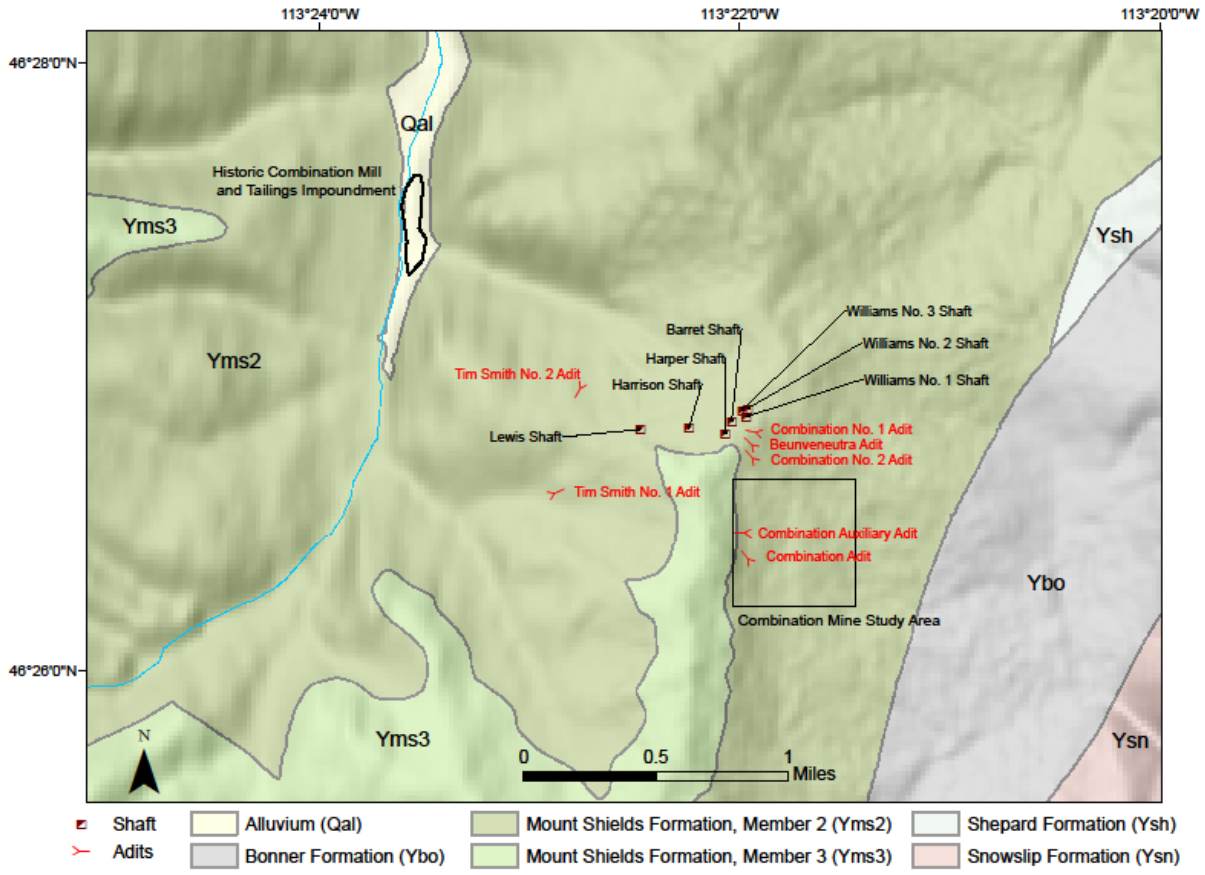

Figure 2: Geologic map of Combination Mine (geologic data from the Montana Bureau of Mines and Geology)

The lode at the Combination Mine is a shallow-dipping fissure vein in the host rock of quartzite and cuts bedding at a low angle. The vein was deposited as open-space filling and was not a replacement of the quartzite. Thickness of the vein varies from six-inches to four-feet and dips from 10°-20° SW (Emmons & Calkins, 1913). The ore averaged 17oz of silver per ton and contained 0.3% tungsten (Emmons & Calkins, 1913). Oxidized ore is stained with manganese and iron oxides, and is known to contain many secondary minerals of Pb, Cu, Sb, and As, including at least two new minerals. The mining method used was underground room and pillar that followed the shallow dip of the Combination vein into the mountainside.

1.2. Prior Reclamation

Environmental monitoring and investigations started in 1981 and have continued at various degrees since then (MDEQ-AML, 2012). Historic remediation efforts at the Combination mine include installing a seepage collection and pump back system in 2001, and regrading the waste rock pile. The seepage collection and pump back system consist of two different collection system. The upper collection system collects water from the toe of the waste rock pile, the lower collection system is a french drain downhill from the waste rock pile and road. The lower collection system flows to CPS-1. Both upper and lower seepage collection systems are pumped back into the underground mine pool through the auxiliary adit. The Combination waste rock pile was regraded and capped between 2004-2006 to help improve slope stability and also to consolidate waste. Impacted soil identified previously was combined with the waste rock during the regrading process and a polyvinyl chloride liner was placed over the waste rock pile (Herrera Environmental Consultants, Inc., 2014).

In 2011 a reclamation investigation conducted by Herrera Environmental Consultants and Trihydro Corporation at the request of MDEQ-AML found that metal concentrations in groundwater seepage exceeded the MDEQ risk-based cleanup guidelines or Circular DEQ-7 standards. Concentrations of arsenic, zinc, manganese and copper were above the MDEQ risk-based cleanup guidelines in the majority of seeps sampled, while cadmium, iron and lead exceeded the guidelines in at least one sample. Since regrading and capping the waste rock pile, concentrations of contaminants in the seeps initially decreased but the downwards trend has recently leveled off. Solid samples taken from test pits of the waste rock pile exceeded MDEQ risk based cleanup guidelines for antimony, arsenic, and lead for all samples. Manganese exceeded the guidelines in only one sample (MDEQ-AML, 2012).

Sampling of groundwater seeps has taken place since 2000 and shows that metal concentrations have consistently exceeded the risk based cleanup guidelines. The mine pool water elevation has risen 115 feet since the installation of the seepage collection and pump back system and continues to rise. Previous to the rise in the mine pool water, two seeps (CPS-9, and CPS-10A) were located at a higher elevation than the mine pool water. The location of seeps above the mine pool elevation and the seasonal fluctuation of flow rates of all the seeps have brought into question the influence of the mine pool on the seeps in the area. Due to the uncertainty of the source of the seeps along with the elevated metal concentrations Herrera Environmental recommended removing all 231,200 cubic yards of waste rock located at the Combination Mine (Herrera Environmental Consultants, Inc., 2014). Herrera Environmental also recommended further sampling of the seeps and mine pool to determine if water treatment will be needed to meet the risk based cleanup guidelines.

1.3. Thesis Objectives

The objective of this thesis is to determine if the groundwater seeps located at the Combination mine are recharged by the flooded mine pool, by shallow flow paths through the waste rock pile, or by a combination of both. Figure 3 shows a conceptual hydrologic model of the Combination mine. As shown in Figure 3 the flooded mine pool and mine dump location is known, but the flow paths for groundwater to the seeps are unknown.

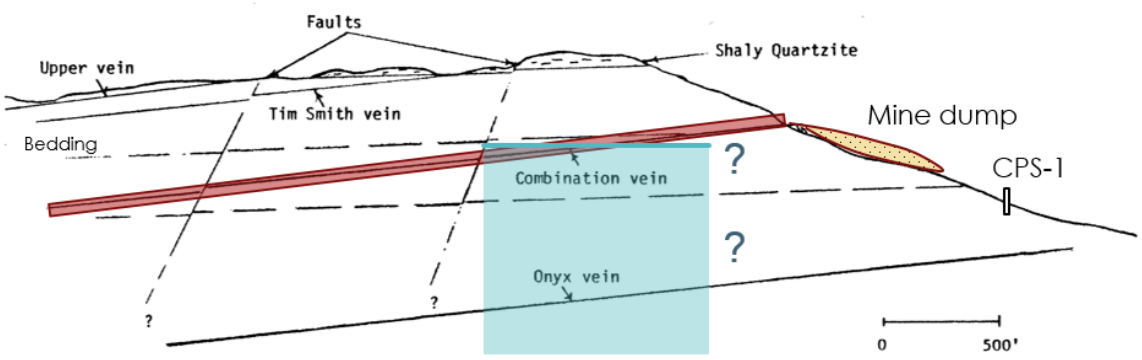

Figure 3: Conceptual hydrologic model showing the flooded mine pool and waste rock of the Combination Mine. Cross section from Zeihen (1985))

Seasonal variability of water isotopes ($\delta^{18}O$, and $\delta^{2}H$) was used to determine if the seeps were originating from local precipitation or from a large reservoir of mine pool water. $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate were measured from the mine pool water, groundwater wells, and seeps to attempt to identify any isotopic difference in the sources of sulfate in these waters. Samples from 3 major seeps were run through inductively coupled plasma atomic emission spectroscopy (ICP-OES) to determine seasonal fluctuation in concentrations. A laboratory leachate test was performed on three different bulk samples of waste rock with the leachate samples analyzed for $\delta^{34}S$ and $\delta^{18}O$ of sulfate and major and trace element chemistry to compare with the seeps and mine pool waters at the field site.

2. Methods

2.1. Field Methods

Field work included collecting samples from the flooded mine pool, eight shallow groundwater wells, eight seeps, and two surface water samples. The mine pool and wells were only sampled twice due to locks being placed to prevent access. The seeps were sampled periodically from late spring to early fall. Only two of the eight seeps continued to flow throughout the summer and fall. Two wells were dry during the fall sampling. Table I shows the sampling dates. Locations of the wells and seeps are shown in Figure 4. Locations of the seeps and wells were taken by Herrera Environmental using a Trimble Global Positioning System (GPS) hand held unit.

A complete set of samples collected in spring and fall of 2014 was analyzed by inductively coupled plasma mass spectrometry (ICP-MS) as part of Herrera's ongoing site investigation. These results were provided to the author.

Table I: Dates samples were collected

Date	Wells	Seeps	Mine Pool	$\delta^{18}O$, $\delta^{2}H$ of water	$\delta^{18}O$, $\delta^{34}S$ of sulfate	ICP-OES	ICP-MS	Fe speciation
5/8/2014	X	X		X	X		X	
5/9/2014		X	X	X	X		X	
5/21/2014		X			X			
7/19/2014		X		X				
8/3/2014		X		X				
8/16/2014		X		X		X		
8/30/2014		X		X		X		X
9/20/2014		X		X		X		X
10/14/2014		X		X		X		
10/24/2014	X	X	X	X	X		X	

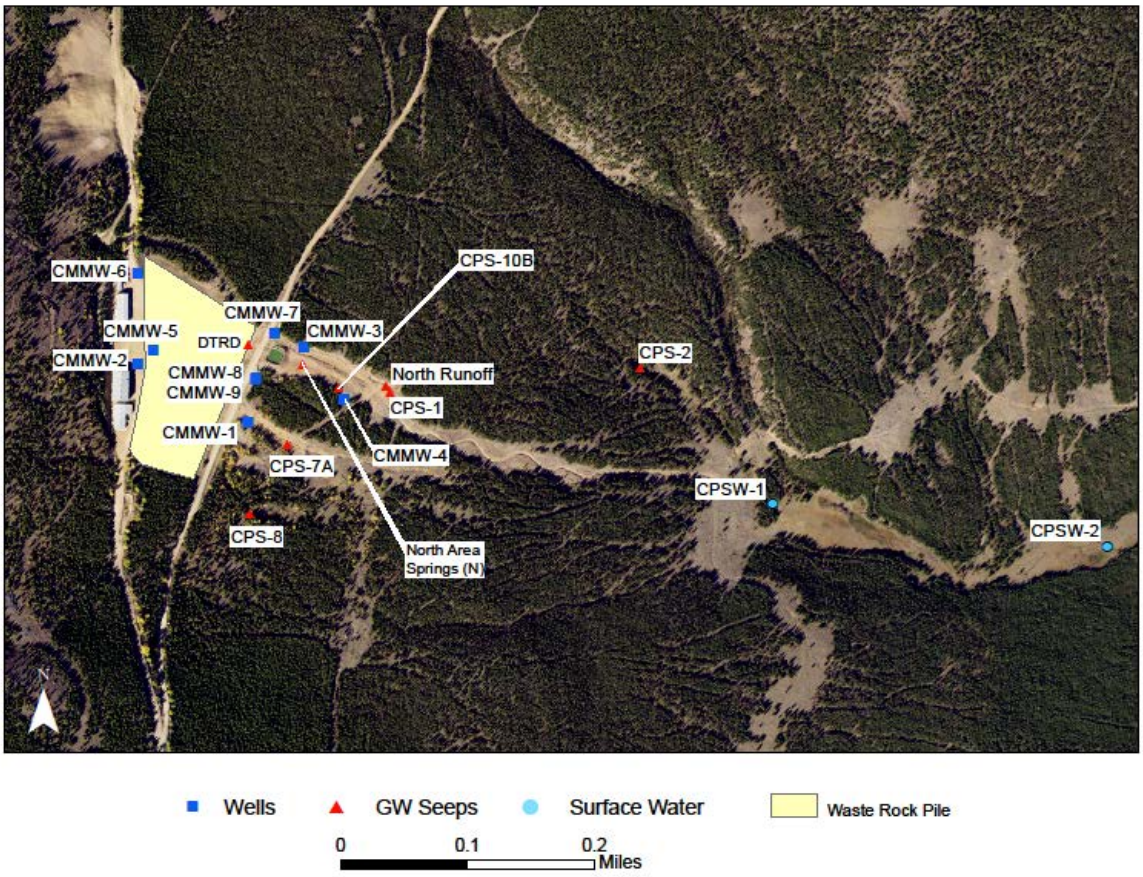

Figure 4: Map of Sample Site Locations

There are nine monitoring wells on site, but one well (CMMW-9) was dry every time sampling occurred. Wells that were sampled varied in depth from 40 feet below ground surface to 100 feet below ground surface. Depth to water and total depth of each well was measured with a water level probe. Three well volumes were purged with parameters (pH, SC, temperature, and dissolved oxygen) taken at approximately every well volume that was purged. A plastic bailer was used to purge the wells. After three well volumes were purged from the well, samples were collected.

During the May sampling event there were eight groundwater seeps. These seeps include seepage collection point CPS-1 which is a sump and access point for the lower seepage

collection system previous installed. Shallow groundwater at the toe of the waste rock pile is collected and pumped back into the mine pool through the auxiliary adit.

Well samples on May 8, 2014 were collected using either a pressure bailer with an attached filter or by pouring from a bailer into a single use hand vacuum filter (0.45 micron). When the pressure bailer was used a 0.45 micron high flow filter was attached to the bailer after water was extracted from the well and then a hand pump was attached to the other end of the bailer to pressurize the bailer and aid in water flowing through the filter. When the single use hand vacuum filters were used water was poured from the bailer into the top of the vacuum filter. Stable water isotope samples were collected after filtration in clear glass 10 milliliter (mL) vials with a plastic conical cap to prevent air bubbles. The bottles were sealed with no head space or air bubbles. Samples for $\delta^{18}O$, $\delta^{34}S$ of sulfate were collected in plastic bottles after filtration. Various size plastic bottles were used to collect samples but at a minimum 250 mL was collected.

Samples from the seeps on May 8, 2014 and May 9, 2014 were collected after pH, specific conductance, temperature, and dissolved oxygen were measured. Flows for all the seeps were measured by filling a 5-gallon bucket and using a stop watch to record the time required. The samples were filtered using the same methods as the groundwater samples from 5/8/2014. The same bottle types were used for sample collection.

The mine pool was sampled on May 9, 2014 by having employees from TriHydro and Herrera Environmental walk into the adit and fill two one-gallon plastic bottles. Once the bottles were brought out of the adit the water was poured into a pressure bailer with a 0.45 micron filter and filtered into a new 250 mL plastic bottle. A duplicate sample was taken

from the mine pool for $\delta^{18}O$, $\delta^{34}S$ of sulfate analyses. Samples for stable water isotopes were collected after filtering into a 10 mL clear glass vial with a plastic conical lid.

Two seeps were resampled on May 21, 2014 due to sample labels being destroyed during shipment. A 60-mL high density polyethylene (HDPE) syringe was used to collect the sample. The sample was filtered into a 250 mL bottle using a 0.2 micron filter.

On July 19, 2014 and August 3, 2014 only three seeps were still flowing. These three seeps were sampled for stable water isotopes and flow rate. Stable isotope samples were collected non-filtered in 88 mL HDPE plastic bottles that were rinsed three times. The bottle was submerged in the seep and the cap was placed on it immediately afterwards. Care was taken to ensure no head space or air bubbles were present in the sample bottle. These samples were filtered using a high density polyethylene syringe with a 0.2 micron PES syringe filter before analyses.

From August 16, 2014 through October 14, 2014 samples from flowing seeps were collected using a 60-mL HDPE syringe that was rinsed three times with the site water. The syringe was placed into the seep to collect the sample. Stable water isotope samples were filtered into a 10 mL glass vial using a 0.20 micron polyethersulfone (PES) syringe filter. The 10 mL vial had a plastic conical cap that prevented entrapped air. Care was taken to ensure no air bubbles or head space were present in the 10 mL bottles. Samples taken for ICP-OES analysis were collected and filtered in the same way as the stable water isotope samples but were placed in a 60 mL Nalgene bottles and preserved with 1% nitric acid (trace metal grade). Samples collected for iron speciation were done the same as the ICP-OES samples but were preserved with 1% hydrochloric acid instead of nitric acid. Before the samples were collected a Hydrolab MS-5 was used to measure dissolved oxygen, specific conductance, pH, and oxidation-reduction

potential. The Hydrolab MS-5 was calibrated before each use. Zobell's solution was used to calibrate the oxidation-reduction potential to read Eh (relative to the standard hydrogen electrode). The pH was calibrated with pH 4 and pH 7 buffers.

On October 24, 2014, wells were sampled for stable water isotopes, ICP-OES analysis and $\delta^{34}S$, $\delta^{18}O$ of sulfate. The sampling methods followed the previous well sampling methods for measuring well depth, purging wells, and measuring parameters approximately every well volume. Samples for $\delta^{34}S$, $\delta^{18}O$ of sulfate were collected unfiltered into one or two 100mL plastic bottles depending on the sulfate concentration from the previous spring. The samples were later filtered in the lab using a vacuum filter and previously weighed filters. A Hydrolab MS-5 was used to measure pH, Eh, DO, temperature, and specific conductance before samples were collected. Two seeps were still flowing at this time and samples for ICP-OES and $\delta^{34}S$, $\delta^{18}O$ of sulfate were collected.

The mine pool was sampled a second time on October 24, 2014. In order to enter the adit and collect the mine pool sample a hard hat, high visibility vest, and a rescue breather was worn. The main tunnel in the adit, which slopes gently to the west, was followed for approximately 750 feet until the mine pool water was encountered. Parameters were measured in several locations that could be reached to check for spatial variability in the mine pool. Samples for ICP-OES and stable water isotopes were collected and filtered. A 5-gallon bucket was filled and covered with a lid for analysis for $\delta^{34}S$, $\delta^{18}O$ of sulfate.

Alkalinity was measured in the field on August 8, 2014 using unfiltered seep samples. A graduated cylinder was used to measure 100.0 mL of sample and then the sample was transferred to a 250 mL Erlenmeyer flask. The sample was titrated to a pH 4.5 using a HACH digital titrator with a 0.16 normal sulfuric acid cartridge. While titrating the sample was stirred continuously

using a portable magnetic stirrer. Bromcresol green-methyl red pH indicator was added to the sample before titration to determine the end point of pH 4.5.

2.2. Experimental Methods

Three 5-gallon buckets of waste rock samples from the main Combination Mine dump were provided by Trihydro Corporation. Each bucket was from a separate sample location in the waste rock pile. The samples were sorted by hand and material that ranged in size from silt to gravel was placed into a humidity cell to conduct a leachate experiment (Figure 5). Approximately 1-kilogram (kg) of waste rock sample was added to each cell along with deionized water to cover the waste rock sample. The deionized water was allowed to set for one week at which time the cells were drained. Due to inadequate water recovery another 0.5-kg of waste rock sample along with additional deionized water was added to each cell. After an additional three days the cells were drained and leachate samples were collected for ICP-OES in 60 mL Nalgene bottles and preserved with 1% nitric acid (trace metal grade), and for $\delta^{34}S$, $\delta^{18}O$ of sulfate in 100-mL HDPE bottles.

Figure 5: Leachate Experimental Setup

2.3. Analytical Methods

2.3.1. This Study

Analytical methods include stable water isotope ($\delta^{18}O$, and $\delta^{2}H$), $\delta^{34}S$, $\delta^{18}O$ of sulfate, ICP-OES, iron speciation, and sulfate concentration.

2.3.1.1. Chemical Analysis

Samples and field duplicate samples were analyzed for major and trace elements by Inductively Coupled Plasma-Optical Emission Spectroscopy by the author at Montana Tech (Butte, MT). A Thermo-Scientific iCAP 6300 Duo ICP Spectrometer was used using EPA Method 200.7. Samples collected in the field and preserved with nitric acid were diluted by a factor of 10 before ICP-OES analysis.

Iron speciation was performed on samples preserved with hydrochloric acid using a HACH 2010 spectrophotometer and the ferrozine method of Stookey (1970). Samples were diluted prior to analyses. Total iron was analyzed by first adding a pH buffer and 0.25 mL of hydroxylamine-HCl along with 0.5 mL of ferrozine. This sample was then placed in the HACH spectrophotometer set to a wave length of 562 nanometers. Iron (II) was analyzed by adding a pH buffer and the 0.5 mL of ferrozine without the hydroxylamine-HCl. Iron (III) was calculated by subtracting iron (II) from the total iron.

Sulfate concentration analyses were performed using the HACH Method 8051 on unpreserved, filtered samples. Barium chloride powder packets were added to the sample in order to form a colloidal suspension of $BaSO_4$(s), which was quantified with the spectrometer. Dilution of samples was necessary in order to be within the linear range of the spectrophotometer (1-100 mg/L SO_4).

2.3.1.2. Isotopic Analysis

Isotopic analysis for δ^2H and $\delta^{18}O$ of water was performed at Montana Tech using a Picarro L1102-I CRDS water isotope analyzer. The isotope analyzer was calibrated using USGS 47 and USGS 48 isotope standards. The estimates precision is ±0.2‰ for $\delta^{18}O$ and ±1‰ for δ^2H.

To analyze the stable isotope composition of sulfate, dissolved SO_4 was first precipitated at the Montana Tech lab by addition of 3x excess of $BaCl_2$. The pH of the sample was first lowered to <3 by addition of HCl to prevent precipitation of $BaCO_3$. The white $BaSO_4$ precipitate was filtered, rinsed several times with DI water, and dried at ≥ 60°C overnight. The samples were then sent to University of Nevada-Reno for analysis of $\delta^{34}S$ and $\delta^{18}O$. A Micromass IsoPrime stable ratio mass spectrometer was used. Estimated precision is ±0.1% for $\delta^{34}S$-sulfate and ±0.2% for $\delta^{18}O$-sulfate.

3. Results

3.1. Groundwater Elevation

In 2014, the flooded mine pool water in the Combination Mine was up gradient from the groundwater seeps sampled (Figure 6), and was approximately 50 feet higher in elevation than the road at the base of the mine waste repository. As shown in Figure 6, groundwater generally flowed downhill in an easterly direction.

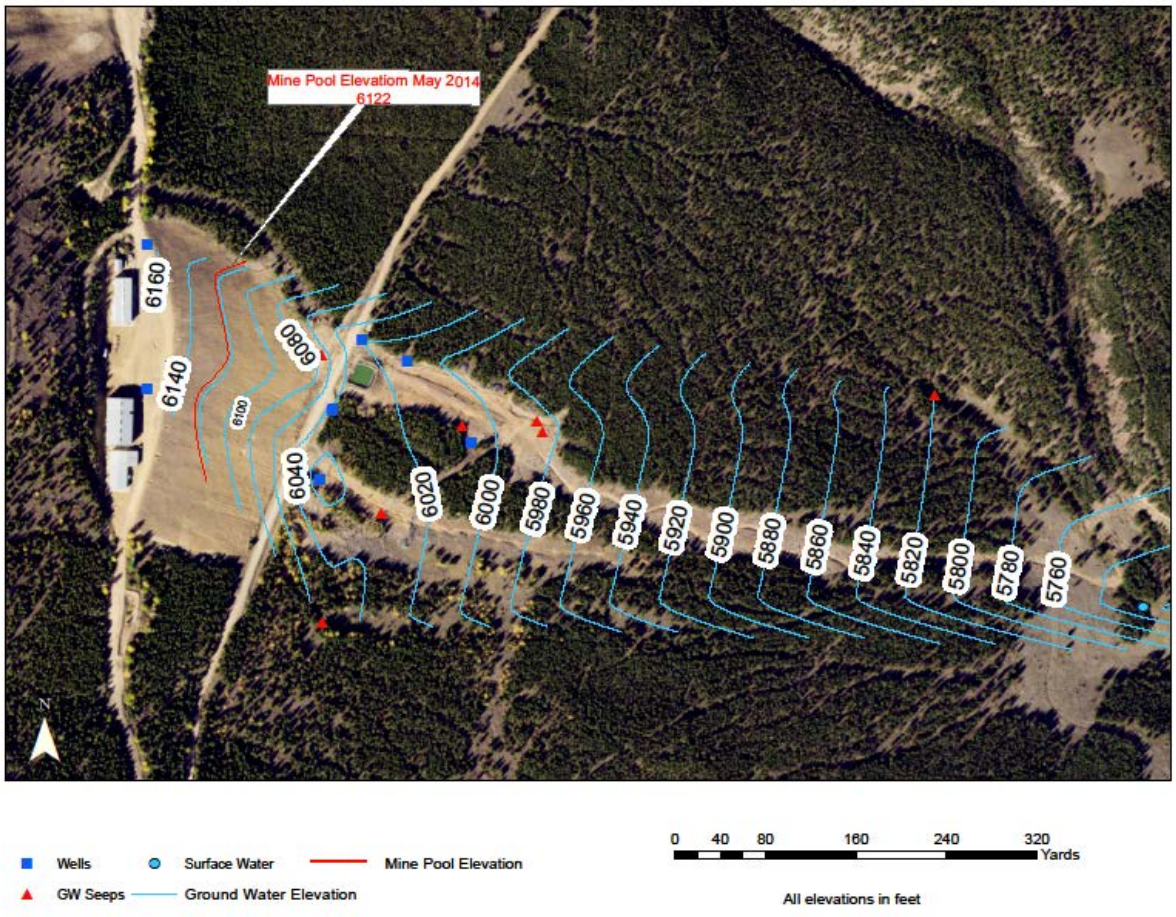

Figure 6: Combination Mine Groundwater Elevation (5/11/2014)

3.2. Geochemistry

Table II shows field alkalinity and iron speciation results. Most of the dissolved iron at CPS-1 is ferric (+3) indicating oxic conditions in the groundwater collection system. This agrees with the high dissolved oxygen measured at CPS-1 year-round. Field parameters and ICP-MS data, provided by Herrara, for surface water and groundwater seeps are shown in Table III. Concentrations of sulfate range from a high of 333 mg/L at CPS-1 to a low of 4.3 mg/L at CPS-2. DTRD and CPS-1 have the lowest pH and highest concentrations of cadmium, copper, manganese, and zinc. The mine pool water has a higher pH and lower concentration of cadmium, copper, manganese, and zinc. Groundwater field parameters and ICP-MS data are shown in Table IV. Concentrations of sulfate range from a high of 746 mg/L at CMMW-2 to a low of 2.1 mg/L at CMMW-1. CMMW-7 has the highest concentration of cadmium, copper, manganese and zinc. Figure 7 compares the sulfate, cadmium, copper concentration and pH in May 2014 for the surface water, groundwater seeps, and groundwater. As shown in Figure 7, CPS-1 concentrations of sulfate, cadmium and copper are higher than most other groundwater seeps in the area.

Table II: Field alkalinity and iron speciation

Location	Date Sampled	Alkalinity (mg/L CaCO3)	Iron II (mg/L)	Iron III (mg/L)
CPS-1	8/16/2014	— —	— —	— —
CPS-1	8/30/2014	— —	0.059	0.751
CPS-1	9/20/2014	— —	0.0145	0.263
CPS-2	8/16/2014	23.2	— —	— —
CPS-8	8/30/2014	20.8	— —	— —

Table III: Surface water and groundwater seeps field parameters and ICP-MS data

Location	Date Sampled	Discharge (gpm)	SC (µS/cm)	Dissolved Oxygen (mg/L)	pH	Sulfate (mg/L)	Sb (mg/L)	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Mn (mg/L)	Zn (mg/L)
CPS-1	5/8/14	18.8	412	12.4	4.42	333	B.D	B.D	0.177	12.9	B.D	0.0003	3.64	13.7
CPS-2	5/9/14	4	34	10.6	6.32	4.3	0.003	0.0034	0.0002	0.0222	1.65	0.0065	0.0382	0.0223
CPSW-1	5/9/14	100	47	10.8	7.11	17.9	0.0222	0.0023	0.0034	0.112	0.003	0.0034	0.0194	0.29
CPSW-2	5/9/14	150	58	11.6	7.12	22.4	0.0024	0.0019	0.0028	0.118	0.871	0.0022	0.0245	0.289
CPS-7A	5/9/14	0.3	128	12.7	5.08	76	0.0333	0.0099	0.037	1.37	1.59	0.0595	0.138	3.31
CPS-8	5/9/14	0.5	85	13.0	6.22	33.8	0.0031	0.002	0.0044	0.094	0.858	0.0023	0.0237	0.281
CPS-10B	5/9/14	0.8	341	9.5	4.23	251	B.D	B.D	0.128	8.96	0.098	0.0004	2.35	B.D
North Runoff	5/9/14	6.3	97	11.8	6.57	53.9	0.0016	0.0017	0.0177	0.855	1.21	0.0029	0.163	1.39
Wet Vault	5/8/14	NA	313	12.1	5.17	259	B.D	B.D	0.0951	6.37	1.1	0.0008	1.93	7.82
North Area Spring (N)	5/9/14	4	64	11.6	5.88	24.4	0.0018	0.0057	0.0072	0.599	4.09	0.0121	0.191	0.426
DTRD	5/8/14	0.7	219	16.7	4.21	193	0.0323	0.0212	0.175	14.9	3.22	0.0536	4.15	14.5
Mine Pool	5/9/14	NA	112	16.7	7.38	24.3	0.11	0.023	0.0425	2.68	2.87	0.169	1.07	2.47
Mine Pool	10/24/14	NA	264.1	14.3	6.89	96.3	0.0603	0.00094	0.0522	2.34	0.064	0.0088	1.39	3.25

B.D. – below detection limits
SC –specific conductance

Table IV: Groundwater field parameters and ICP-MS data

Location	Date Sampled	SC (µS/cm)	Dissolved Oxygen (mg/L)	pH	Sulfate (mg/L)	Sb (mg/L)	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Mn (mg/L)	Zn (mg/L)
CMMW-1	5/8/14	85	9.26	6.31	2.2	0.0013	0.0022	0.0002	0.024	B.D	0.00038	0.0065	0.012
CMMW-1	10/24/14	94	6.06	7.83	2.1	0.0005	0.0012	B.D	B.D	B.D	B.D	0.0052	0.006
CMMW-2	5/8/14	--	--	--	181	0.0532	0.0675	0.006	0.499	0.52	0.0174	0.101	0.666
CMMW-2	10/24/14	1411	2.73	6.01	746	0.0616	0.0916	0.0108	0.378	0.428	0.0142	0.225	1.29
CMMW-3	5/8/14	549	14.32	4.67	476	B.D	0.0009	0.264	21.7	0.088	0.00065	6.84	21.0
CMMW-3	10/24/14	816	8.66	5.72	346	B.D	0.0015	0.0501	1.62	0.208	0.00018	1.45	4.02
CMMW-4	5/8/14	355	10.98	4.63	268	B.D	0.0005	0.104	6.02	0.123	0.00018	1.78	7.45
CMMW-4	10/24/14	310	8.68	4.99	154	B.D	0.0011	0.03	1.12	B.D	B.D	0.388	2.17
CMMW-5	5/8/14	158	9.81	5.21	108	0.0009	0.0005	0.136	6.05	B.D	0.002	3.69	10.4
CMMW-6	5/8/14	54	16.85	7.82	6.6	0.0011	0.0013	0.0009	0.040	0.158	0.00061	0.0093	0.038
CMMW-6	10/24/14	1410	5.58	6.04	18.5	0.0014	0.0025	0.0027	0.048	B.D	B.D	0.463	0.077
CMMW-7	5/8/14	591	11.19	4.31	503	B.D	0.0006	0.373	31.9	B.D	0.002	9.35	29.7
CMMW-8	5/8/14	712	24.66	5.25	614	B.D	B.D	0.156	6.61	B.D	0.00025	4.10	11.9
CMMW-8	10/24/14	999	7.7	5.41	636	B.D.	0.0005	0.111	2.17	B.D.	B.D.	2.53	7.330
CMMW-9	5/9/14	317	17.15	5.6	233	B.D.	0.0006	0.0023	0.016	B.D.	.00029	0.016	0.122
CMMW-9	10/24/14	--	--	--	250	B.D.	0.0006	0.0039	0.055	B.D.	B.D.	0.023	0.227

B.D. – below detection limits
-- indicates not measured
SC –specific conductance

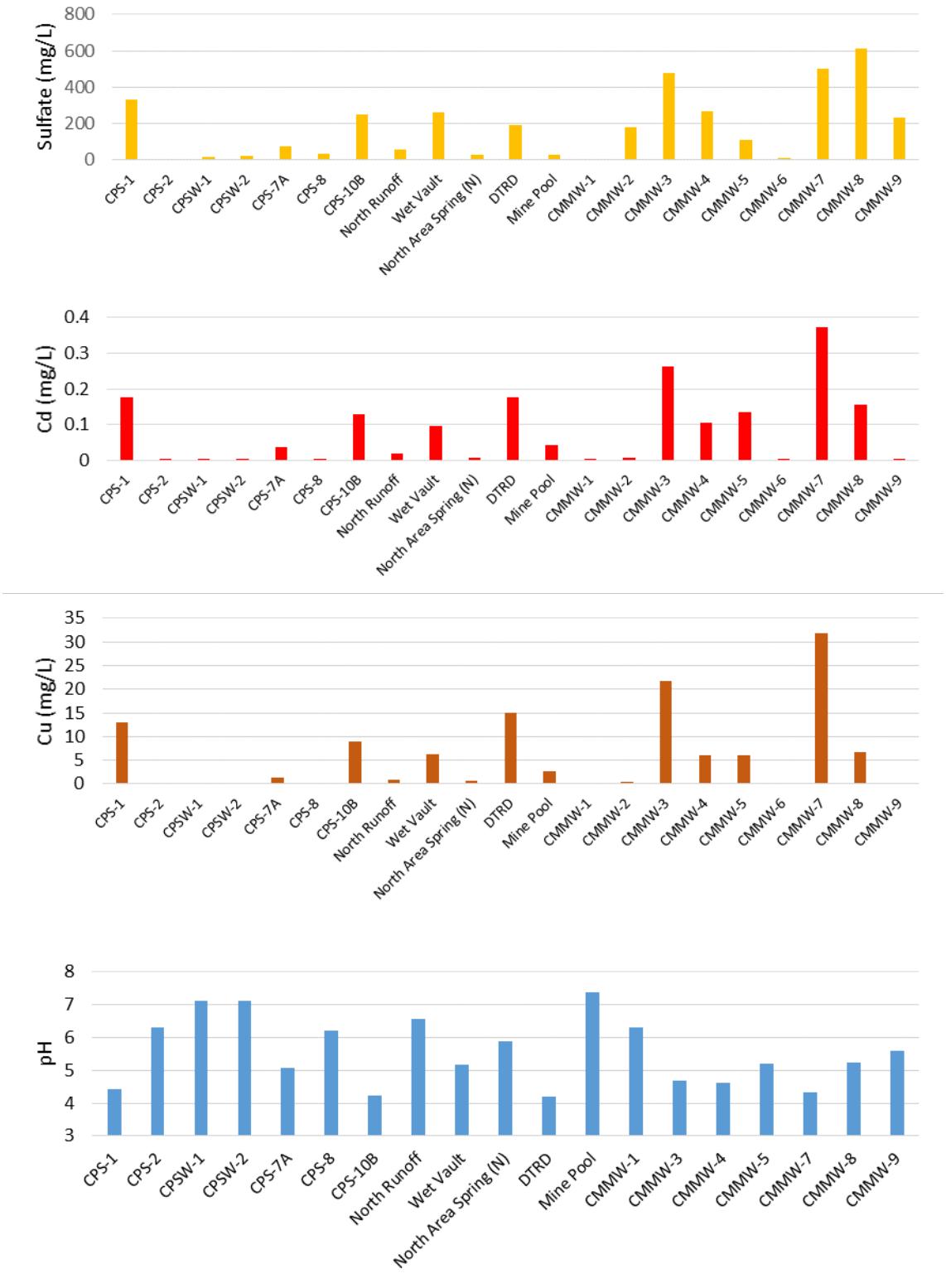

Figure 7: Sulfate, Cadmium, Copper Concentration and pH, May 2014

Samples were collected from groundwater seeps to track temporal changes from 16 August 2014 through 24 October 2014. Only three groundwater seeps were flowing during this time period and one of the three was dry during the last sample event. As shown in Table V concentrations of most solutes in CPS-1 increased slightly during the two-month sampling period. Figure 8 shows that as flow decreased calcium and magnesium concentration increased slightly while the copper, manganese, and zinc remained relatively constant.

Table V: CPS-1 ICP-OES data (adjusted for dilution)

Location	Date Sampled	Discharge (gpm)	As (mg/L)	Ca (mg/L)	Cd (mg/L)	Co (mg/L)	Cu (mg/L)	Fe (mg/L)	Mg (mg/L)	Mn (mg/L)	Zn (mg/L)
CPS-1	8/16/14	2.17	0.007	38.1	0.133	0.030	11.4	0.014	21.2	3.38	10.0
CPS-1	8/30/14	3.10	0.001	36.5	0.124	0.029	10.9	0.013	20.3	3.22	9.53
CPS-1	9/20/14	1.99	B.D	38.9	0.134	0.032	11.5	0.018	21.8	3.45	10.1
CPS-1	10/14/14	1.33	B.D	43.1	0.148	0.035	12.5	0.018	24.1	3.82	11.0
CPS-1	10/24/14	1.57	0.004	45.7	0.156	0.034	13.0	0.046	25.5	4.00	11.6

B.D. – below detection limits

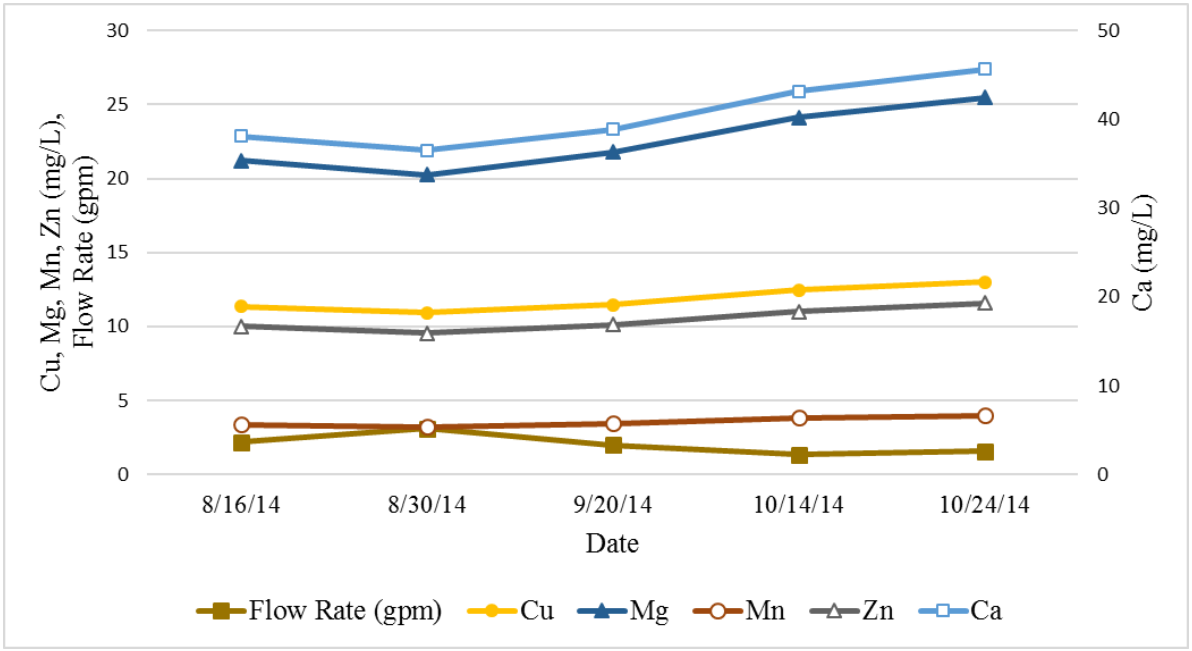

Figure 8: CPS-1 Temporal Changes

CPS-2 did not have measureable flow during the sampling time, but a pool of water was still present until after 14 October 2014 when it dried out completely. Concentrations of selected analytes are shown in Table VI. CPS-2 concentrations were lower than CPS-1 except for iron which was higher in CPS-2. Manganese concentration decreased throughout the sampling period while calcium concentration fluctuated (Figure 9).

Table VI: CPS-2 ICP-OES data (adjusted for dilution)

Location	Date Sampled	As (mg/L)	Ca (mg/L)	Cd (mg/L)	Co (mg/L)	Cu (mg/L)	Fe (mg/L)	Mg (mg/L)	Mn (mg/L)	Zn (mg/L)
CPS-2	8/16/14	0.007	5.14	B.D	0.005	B.D	0.098	1.86	0.028	0.002
CPS-2	8/30/14	B.D	3.94	B.D	0.006	B.D	0.329	1.51	0.031	0.003
CPS-2	9/20/14	B.D	4.69	B.D	0.004	B.D	0.127	1.74	0.021	0.005
CPS-2	10/14/14	B.D	4.38	B.D	0.004	B.D	0.072	1.62	0.009	0.005

B.D. – below detection limits

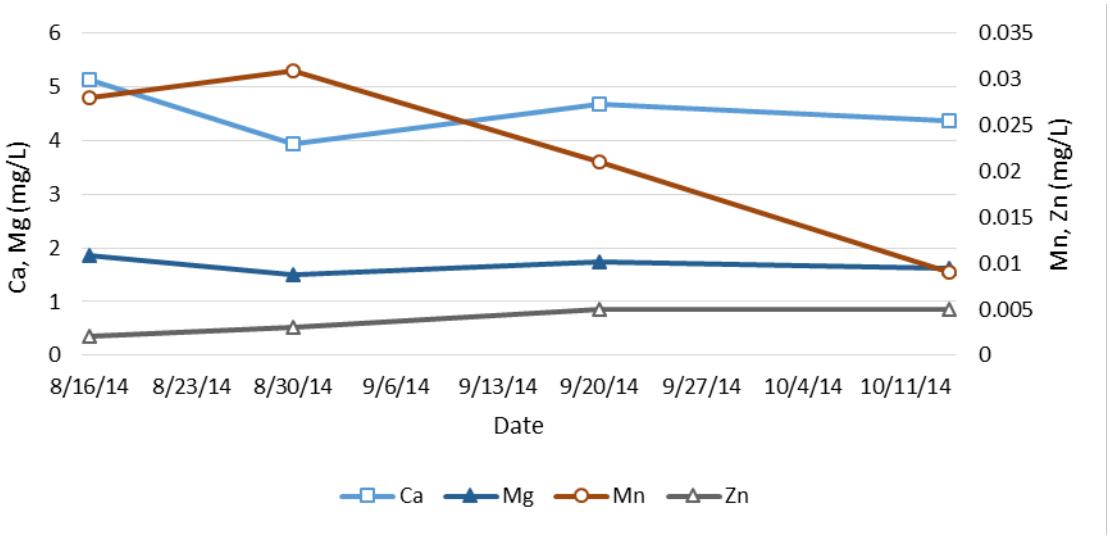

Figure 9: **CPS-2 Temporal Changes**

CPS-8 had water present throughout the sampling period. Table VII shows selected concentration changes over the sampling period. CPS-8 had lower concentrations of the selected analytes than CPS-1 but higher calcium, magnesium, manganese, and zinc than CPS-2. During the course of the study period zinc concentration increased (Figure 10). Manganese

concentration increased while zinc concentration decreased for the last sample analyzed, the other analytes remained relatively constant.

Table VII: CPS-8 ICP-OES data (adjusted for dilution)

Location	Date Sampled	As (mg/L)	Ca (mg/L)	Cd (mg/L)	Co (mg/L)	Cu (mg/L)	Fe (mg/L)	Mg (mg/L)	Mn (mg/L)	Zn (mg/L)
CPS-8	8/16/14	B.D	6.74	B.D	0.003	B.D	0.040	3.15	0.018	0.112
CPS-8	8/30/14	B.D	8.16	B.D	0.003	B.D	0.056	3.74	0.031	0.129
CPS-8	9/20/14	B.D	7.41	B.D	0.003	B.D	0.034	3.42	0.023	0.148
CPS-8	10/14/14	B.D	7.28	B.D	0.003	B.D	0.044	3.32	0.021	0.172
CPS-8	10/24/14	B.D	7.66	B.D	0.003	B.D	0.211	3.46	0.073	0.113

B.D. – below detection limits

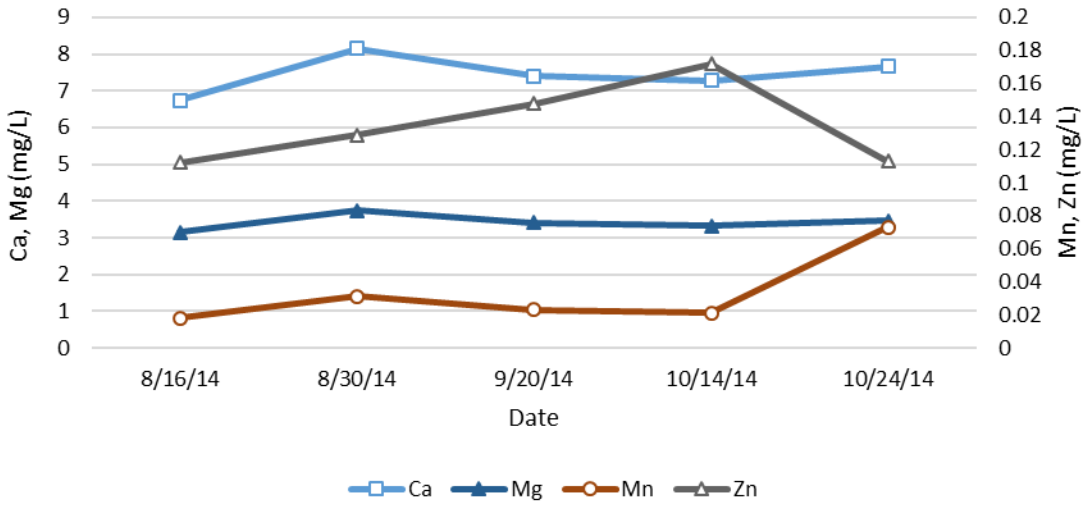

Figure 10: CPS-8 Temporal Changes

Samples from the leachate experiment were analyzed using an ICP-OES (Table VIII). Specific conductance and pH were measured for all samples immediately after the humidity cells were drained. Specific conductance was substantially higher for the leachate experiment compared to the groundwater or seeps sampled in the field, while the pH of the leachate experiment was lower than groundwater and seeps. Leachate collected from the waste rock 1 sample had lower concentrations for most analytes compared to the waste rock 2 and waste rock

3 leachates. Overall, concentrations were higher in the experimental leachate than from the groundwater seeps and wells. Arsenic concentration was low in all three samples.

Table VIII: Waste rock experiment ICP-OES data (adjusted for dilution) [1]

Location	pH	SC (µS/cm)	As (mg/L)	Ca (mg/L)	Cd (mg/L)	Co (mg/L)	Cu (mg/L)	Fe (mg/L)	Mg (mg/L)	Mn (mg/L)	Zn (mg/L)	SO_4 (mg/L)[1]
Waste Rock 1	3.52	2689	B.D	480	0.72	0.30	68.4	0.14	96	49	67.6	700
Waste Rock 2	2.48	4746	0.307	423	3.27	0.62	489	123	205	104	238	5500
Waste Rock 3	3.02	3883	0.022	433	1.49	0.36	450	1.57	122	127	122	3000

[1] – SO4 analysis performed using HACH Method 8051
B.D. – below detection limits
SC –specific conductance

3.3. Water Isotopes

Results for the isotopic composition of δ^2H and $\delta^{18}O$ of the groundwater seeps, mine pool, and wells in the vicinity of the Combination Mine are in Table IX. The results are also plotted along with the Butte Meteoric Water Line (MWL) and the Local Evaporation Line (LEL) (Gammons et al., 2006) in Figure 11. CPS-1 and the mine pool water plot close to each other and their isotopic composition changed very little throughout the study period. All the wells plot close to the Butte MWL, while the majority of groundwater seeps, excluding CPS-1, plot closer to the Butte LEL.

Table IX: Results for stable water isotopic analysis of samples at the Combination Mine

LOCATION	DATE	δ^{18}O-H2O	δ^{2}H-H2O
CMMW-1	10/24/2014	-19.3	-150
CMMW-2	10/24/2014	-17.8	-138
CMMW-3	10/24/2014	-18.2	-141
CMMW-4	10/24/2014	-18.3	-142
CMMW-6	10/24/2014	-18.1	-141
CMMW-8	10/24/2014	-18.2	-140
CPS-1	7/19/2014	-18.2	-141
CPS-1	8/16/2014	-18.2	-141
CPS-1	8/30/2014	-18.2	-141
CPS-1	9/20/2014	-18.2	-141
CPS-1	10/14/2014	-18.1	-141
CPS-1	10/24/2014	-18.2	-141
CPS-1	8/3/2014	-18.2	-141
CPS-10B	5/9/2014	-18.1	-141
CPS-2	5/9/2014	-18.1	-142
CPS-2	7/19/2014	-17.5	-138
CPS-2	8/3/2014	-17.7	-140
CPS-2	8/16/2014	-17.4	-136
CPS-2	8/30/2014	-18.1	-141
CPS-2	9/20/2014	-17.1	-135
CPS-2	10/14/2014	-18.1	-141
CPS-7A	5/9/2014	-18.1	-142
CPS-8	5/9/2014	-18.2	-142
CPS-8	7/19/2014	-17.3	-138
CPS-8	8/3/2014	-17.6	-139
CPS-8	8/16/2014	-18.0	-140
CPS-8	8/30/2014	-18.0	-140
CPS-8	9/20/2014	-18.0	-140
CPS-8	10/24/2014	-17.8	-138
CPS-8	10/14/2014	-18.2	-141
CPSW-1	5/9/2014	-17.9	-141
CPSW-2	5/19/2014	-17.6	-139
MINE POOL	5/9/2014	-18.2	-141
MINE POOL	10/24/2014	-18.3	-142
N. RUNOFF	5/9/2014	-18.1	-142
N. AREA SPRING N	5/9/2014	-18.2	-143

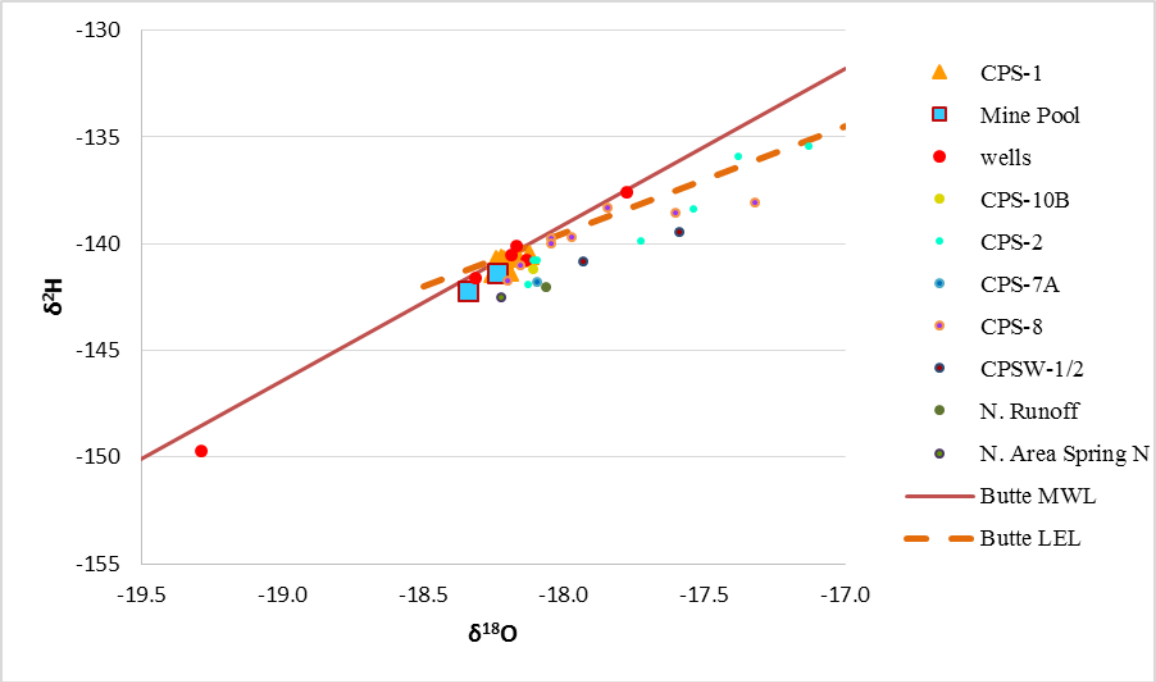

Figure 11: Stable water isotopic data for samples collected plotted against the Butte Meteoric Water Line and Local Evaporation Line.

Further assessment of the stable water isotope composition for the three primary groundwater seeps can be completed using Figures 12, 13, 14. CPS-8 stable water isotope composition (Figure 12) varies throughout the study period and plots closer to the LEL for the majority of samples. CPS-8 samples are also heavier than that of the mine pool samples. CPS-2 stable water isotopes (Figure 13) show a similar trend to CPS-8 with CPS-2 samples being heavier than the mine pool samples and also showing evaporation. In contrast CPS-1 samples (Figure 14) show little change throughout the study period and all plot close to the MWL and mine pool samples.

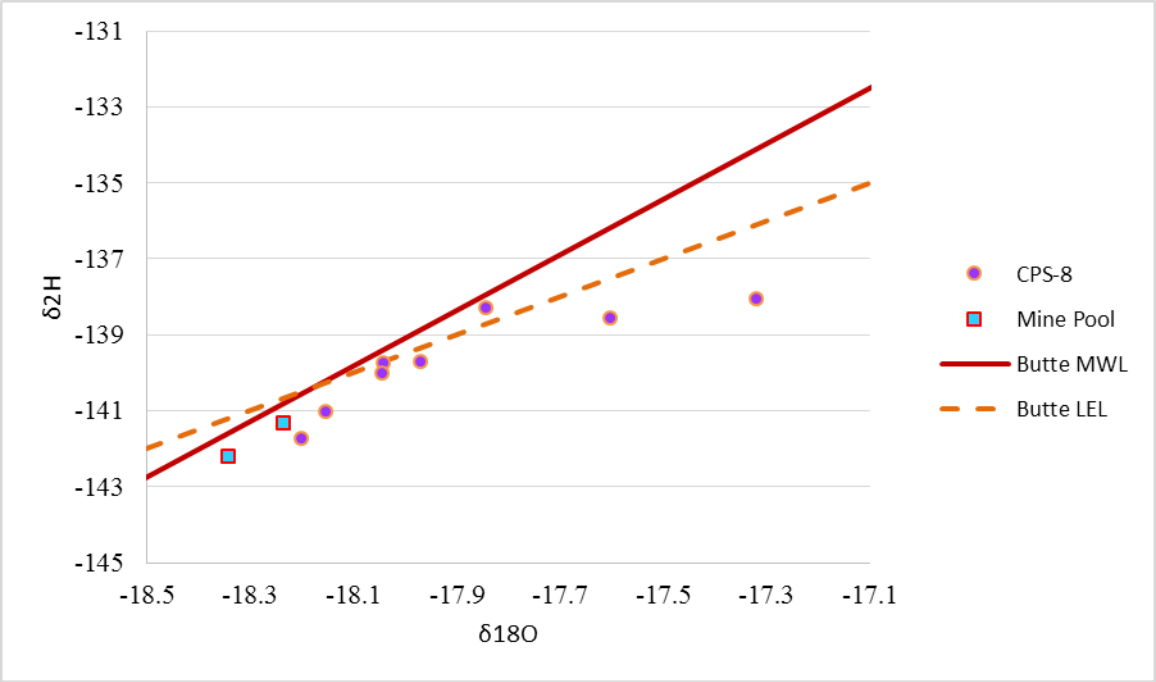

Figure 12: Stable water isotopic data for samples collected from CPS-8 plotted against the Butte Meteoric Water Line and Local Evaporation Line.

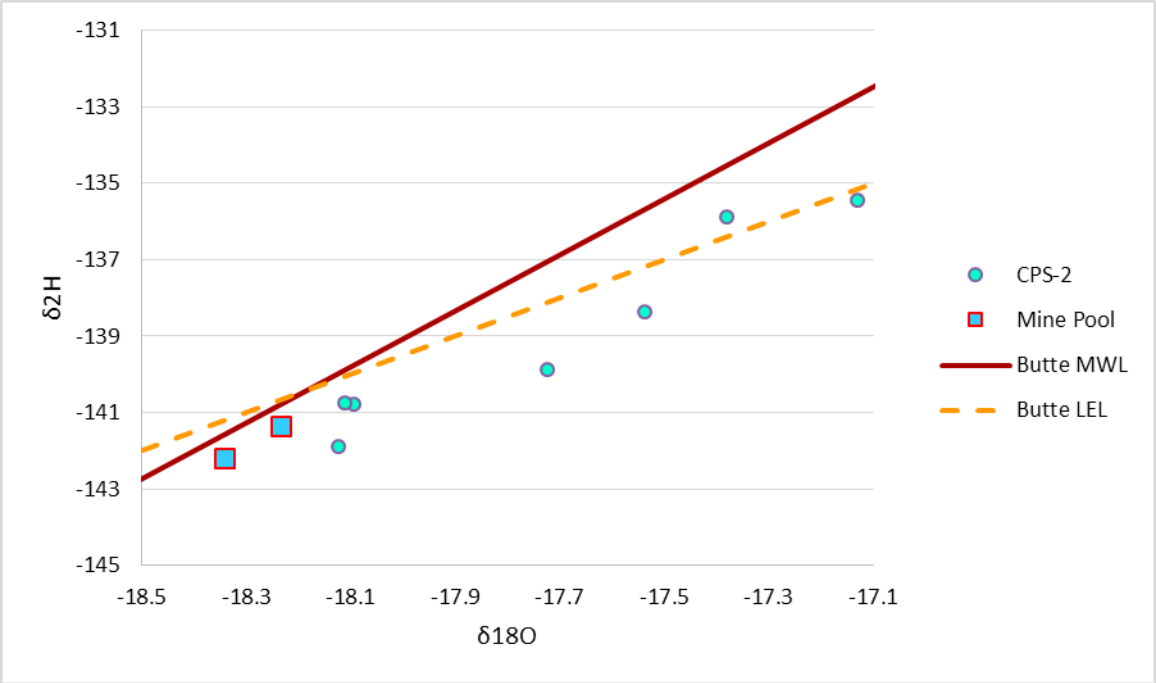

Figure 13: Stable water isotopic data for samples collected from CPS-2 plotted against the Butte Meteoric Water Line and Local Evaporation Line.

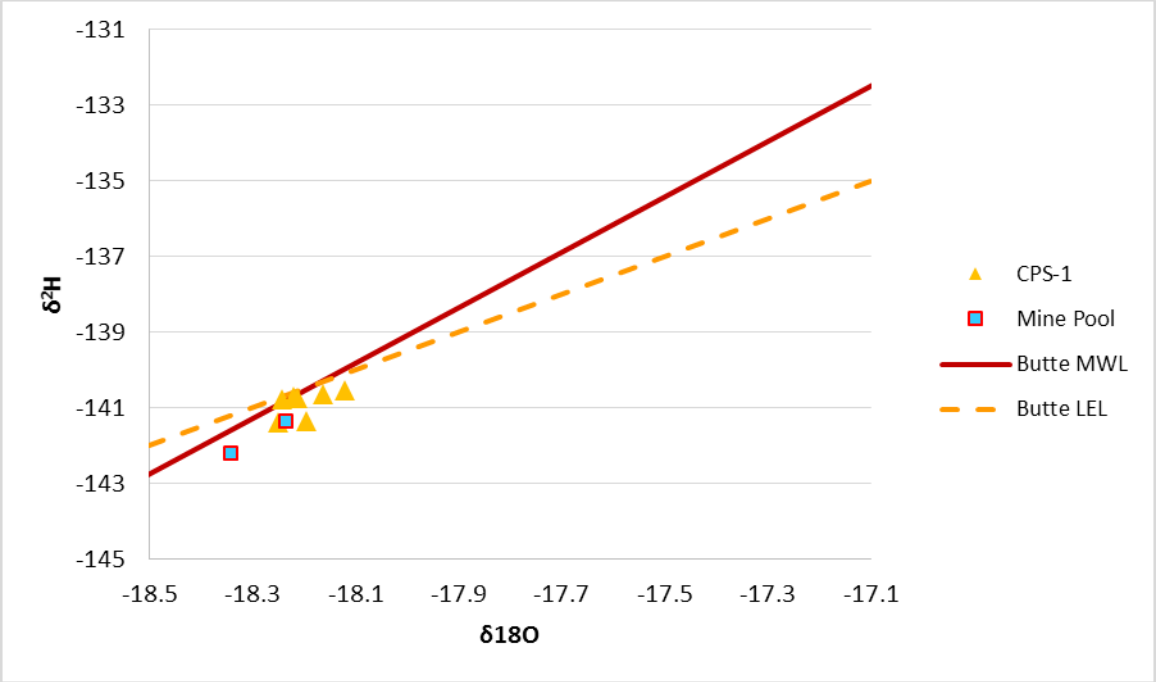

Figure 14: Stable water isotopic data for samples collected from CPS-1 plotted against the Butte Meteoric Water Line and Local Evaporation Line.

3.4. Sulfate Isotopes

Water samples were collected in May and October from groundwater seeps, wells, and the mine pool to analyze $\delta^{34}S$ and $\delta^{18}O$ of sulfate. Samples were also collected from the leachate experiment and analyzed for $\delta^{34}S$ and $\delta^{18}O$ of sulfate. Results of sulfate isotopic analyses for samples collected at Black Pine Mine are shown in Table X. Samples from wells CMMW-1 and CMMW-6 did not have a high enough concentration of sulfate for analysis. During the fall sampling numerous seeps were dry and seep CPS-8 sample lacked sufficient concentration of sulfate for analysis.

Table X: Sulfate isotopes ($\delta^{34}S$ and $\delta^{18}O$) of samples collected at Combination Mine

LOCATION	DATE	$\delta^{34}S$ (‰)	$\delta^{18}O$ (‰)	SULFATE (mg/L)
CMMW-2	5/8/2014	6.9	-7.7	181
CMMW-2	10/24/2014	7.3	-7.8	860
CMMW-3	5/8/2014	5.2	-14.2	476
CMMW-3	10/24/2014	4.8	-12.6	340
CMMW-4	5/8/2014	5.3	-13.7	268
CMMW-4	10/24/2014	5	-11.6	180
CMMW-5	5/8/2014	5.2	-15	108
CMMW-7	5/8/2014	5.1	-14.7	503
CMMW-8	5/8/2014	3.2	-13.2	614
CMMW-8	10/24/2014	2.9	-12.8	740
CPS-1	5/8/2014	5.3	-13.8	333
CPS-1	10/24/2014	5.2	-13.4	320
CPS-10B	5/9/2014	5.2	-13.8	251
CPS-7A	5/9/2014	6.5	-11.3	76
CPS-8	5/9/2014	5.3	-12.9	33.8
CPSW-1	5/9/2014	5.4	-4.8	17.9
CPSW-2	5/9/2014	5	-5.2	22.4
DTRD	5/8/2014	5.4	-13.5	193
MINE POOL	5/9/2014	4.9	-15	24.3
MINE POOL	10/24/2014	4.9	-13.7	90
N AREA SPRING N	5/9/2014	7.4	-4.3	24.4
N RUNOFF	5/9/2014	5.3	-12.6	53.9
WET VAULT	5/8/2014	5.3	-13.8	259
WASTE ROCK 1	—— ——	5.3	-13.4	700
WASTE ROCK 2	—— ——	5.2	-12.1	5500
WASTE ROCK 3	—— ——	5.0	-14.4	3000

Figure 15 shows that the majority of samples collected in this study have $\delta^{34}S$ of dissolved sulfate in a fairly tight range of +4.5 to +5.5 ‰, which is outlined in a red box. This includes the mine pool and CPS-1 samples, as well as the laboratory leachate samples. Samples that plot outside the cluster include CMMW-8, which was consistently lighter in $\delta^{34}S$, and CMMW-2, CPS-7A, and the North Area Spring, which were consistently heavier.

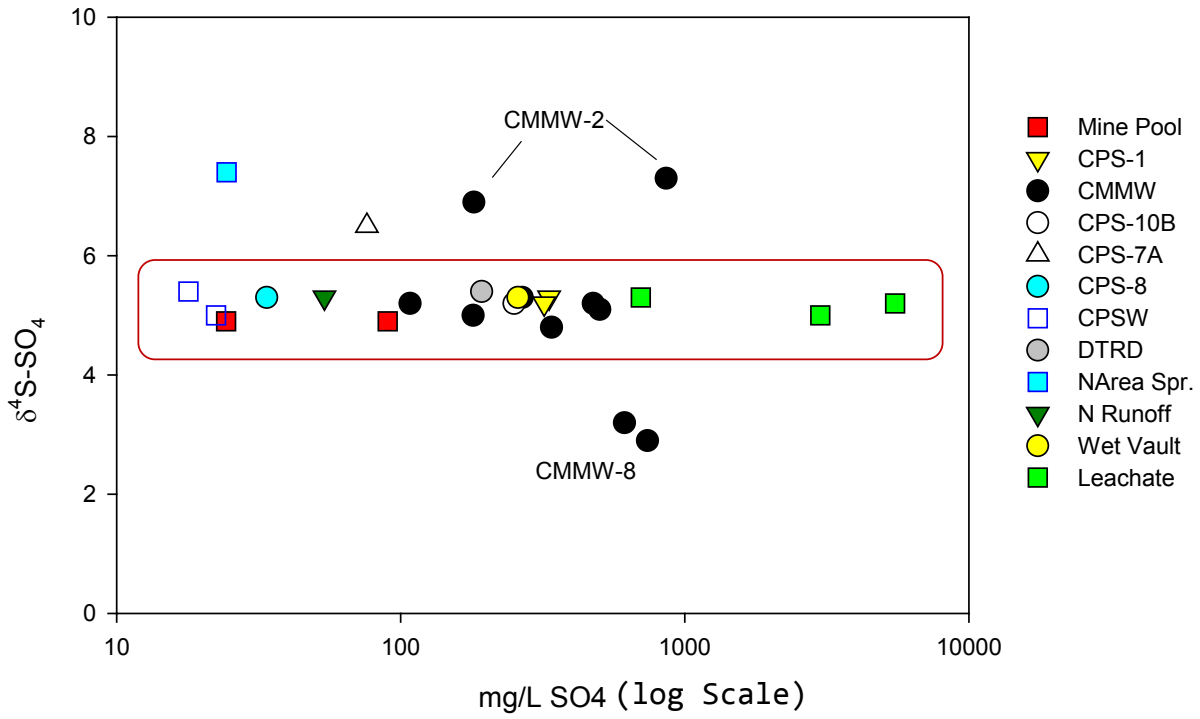

Figure 15: The δ^{34}S-isotopic composition of sulfate vs. sulfate concentration

Figure 16 shows a somewhat broader spread in δ^{18}O-sulfate for the same samples, although again there is a clustering near δ^{18}O = -15 to -11 ‰ which includes the mine pool, CPS-1, and lab leachate samples. Anomalous samples with sulfate δ^{18}O values greater than -10 ‰ include CMMW-2, the two CPSW samples, and the North Area Spring.

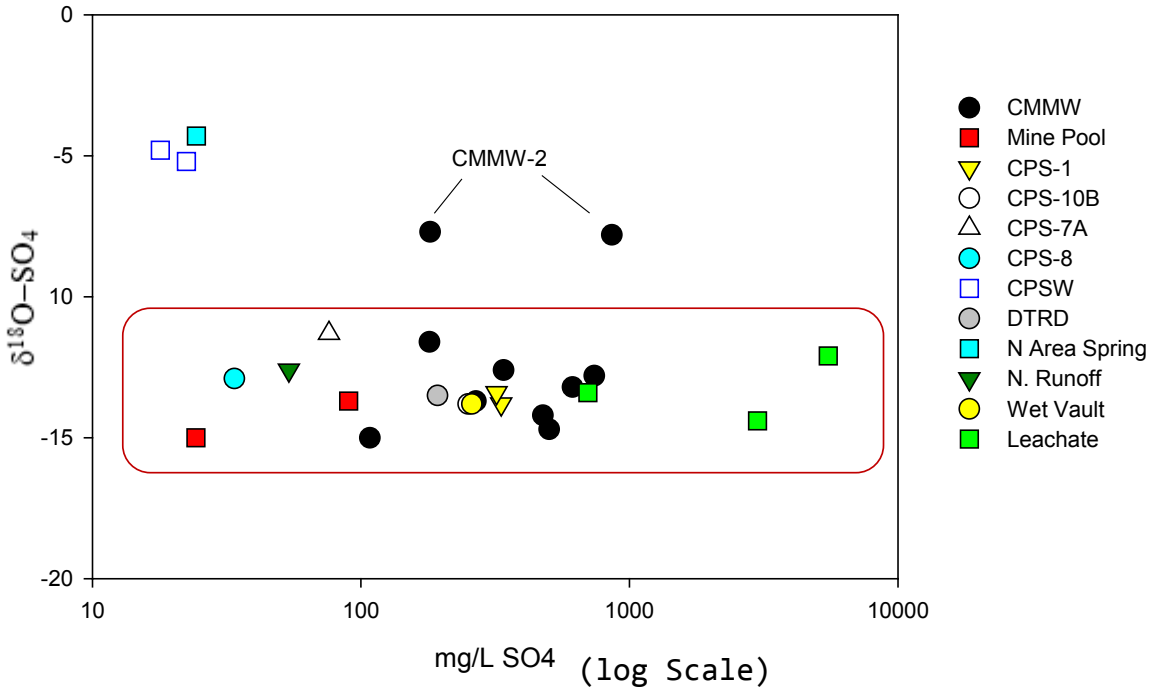

Figure 16: The δ^{18}O-isotopic composition of sulfate vs. sulfate concentration

Figure 17 is an isotope cross-plot of δ^{18}O vs. δ^{34}S of sulfate. Averageδ^{18}O of water shown as a blue dotted line is the average from all samples. The samples which clustered with respect to either isotopic system plot in a tight bundle in the lower-center of the diagram. These samples, circled in dark brown, probably have dissolved sulfate that came from the same source. Outliers include the same samples mentioned above: CMMW-2 and -8,

CPS-7A, the CPSW samples, and the North Area Spring. The reasons for why certain samples plot outside the clustering of data points are not known at this time, although it is worth noting that the CMMW-2 and CMMW-8 samples gave very similar isotopic compositions for both dates of sampling. Therefore, the outliers are probably real, and not an artifact of sampling or analytical errors.

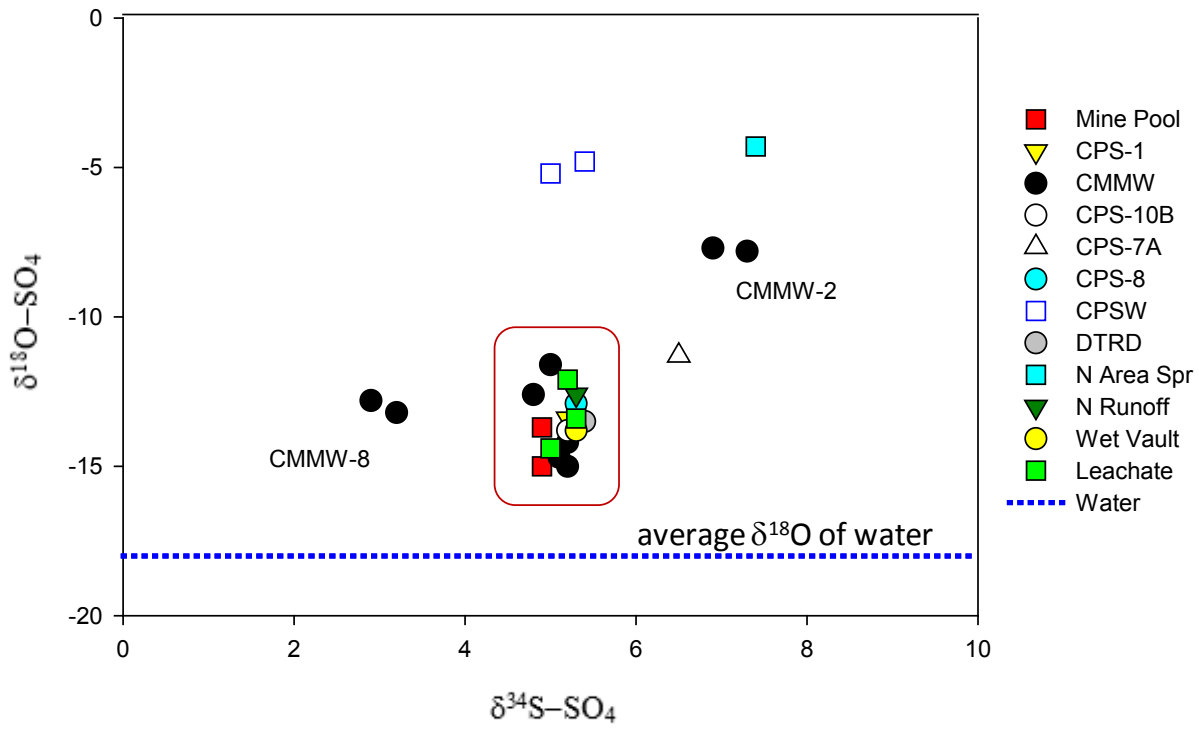

Figure 17: Oxygen vs. sulfur isotopic composition of dissolved sulfate

No clear mixing trends are evident from Figures 15 to 17, nor in plots in which the stable isotopes were plotted vs. reciprocal SO_4 concentration (data not shown here). As discussed by Clark and Fritz (1997), a set of samples obtained by mixing of two endmember sources with distinct isotopic compositions will fall on a straight line when the isotopic compositions are plotted vs. the reciprocal concentrations of the compound in question. The lack of any clear mixing trends suggests that most of the water samples in the Black Pine area inherited their sulfate from a similar source, irrespective of whether they had high or low sulfate concentrations.

4. Discussion

4.1. Geochemistry

Concentrations of analytes of concern in the mine pool are lower than the majority of wells and seeps (Figure 18). CPS-1 and DTRD had the highest concentrations of cadmium, copper, and manganese compared to the other seeps and mine pool. DTRD had the lowest pH of all samples. CMMW-7 had the highest concentration of cadmium, copper, and manganese compared to the other wells and seeps. The wells and seeps with the highest concentrations of analytes of concern (CMMW-7, CMMW-3, CMMW-8, CPS-1, CPS-10B, and DTRD) are all downgradient of the mine pool and downgradient of the waste rock pile. CMMW-6 has low levels of analytes of concern and is located up gradient of the mine pool and waste rock pile. CMMW-1 is another well with low levels of analytes of concern and it is located downgradient of the mine pool and waste rock pile, however CMMW-1 is the farthest south well that was sampled. The majority of samples with high concentration of analytes of concern are clustered in the northern portion of the site immediately downgradient of the waste rock pile and mine pool.

If CPS-1 water starts out as mine pool water, then the composition of the mine water must change as it moves through the bedrock and mine waste before reporting to CPS-1. Cadmium concentration increases by 0.13 mg/L (316% change), copper concentration increases by 10.2 mg/L (381% change), manganese concentration increases by 2.57 mg/L (240 % change), zinc concentration increases by 11.23 mg/L (455% change), and sulfate concentration increases by 308.7 mg/L (1270% change). On the other hand, arsenic concentration decreases from 0.023 mg/L at the mine pool to below detection limits at CPS-1. Iron concentration decreases from 2.87 mg/L to below detection limits at CPS-1. At the same time, the pH changes from neutral (7.38) at the mine pool to acidic (4.42) at CPS-1. These changes in the geochemistry of the water

as it travels from the mine pool to CPS-1 could occur as the water flows through the waste rock piles deposited on the slope. Based on the laboratory leachate results, concentrations of all trace metals, as well as sulfate, should increase when water interacts with the waste rock dump. Importantly, although sulfate concentration would increase, the isotopic composition of sulfate (both S and O) would not change, since the leachate sulfide had a similar isotopic composition as CPS-1 and mine pool sulfate. This agrees with the observations made in the field.

It is important to note the samples collected from the mine pool might not necessarily represent the overall geochemistry of the mine pool water. The mine pool was sampled by accessing the mine through an adit and collecting a water sample where the mine pool was first encountered. Water deeper in the mine shaft could possibly have different geochemistry than where the mine pool sample was collected.

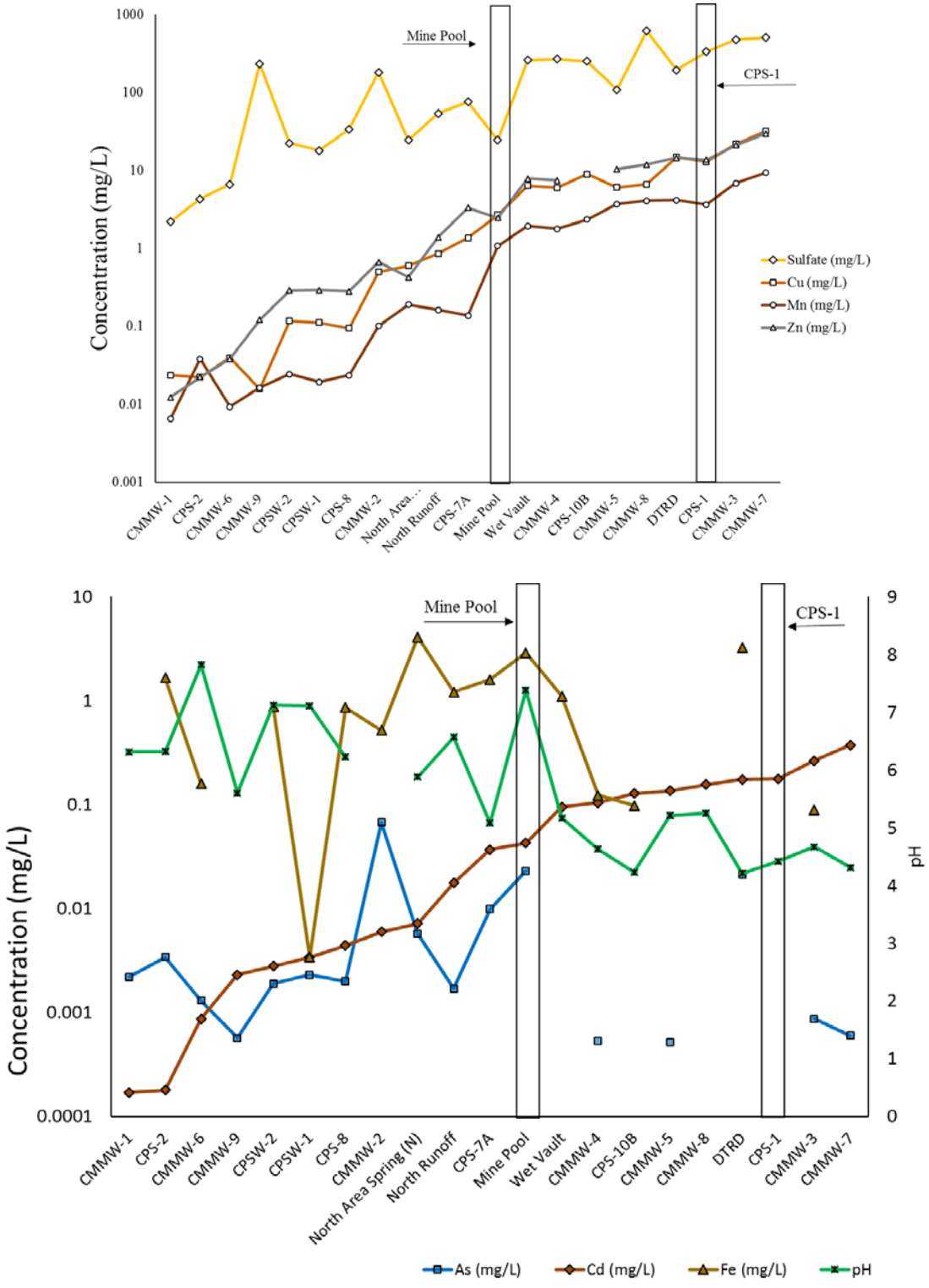

Figure 18: Concentrations and pH of wells, seeps, and mine pool, May 2014

As shown in Section 3.2, very little temporal changes were observed in CPS-2 and CPS-8 with a few exceptions. Manganese concentration had a decreasing trend at CPS-2, and the highest manganese concentration coincides with the high flow period. Zinc concentration had an increasing trend throughout the study period at CPS-8. The remaining analyte concentrations stayed relatively stable throughout the study for CPS-2 and CPS-8.

CPS-1 was the only seep present that had enough flow throughout the season to consistently measure a flow rate and thus calculate loads. Table XI shows the calculated loads (concentration x flow) for CPS-1. Changes in the loads over the sampling period followed changes in the discharge, except for arsenic load, as shown in Figure 19. Arsenic load initially decreased when discharge increased. In the last sampling event arsenic load increased as the discharge increased. The cause of the difference in the arsenic load changes compared to the other analytes is unknown, however the concentration of arsenic in CPS-1 is low. Further investigation into arsenic loading in CPS-1 would need to be conducted in order to determine if arsenic is truly being attenuated during high flow periods and the cause. The fact that loads predominantly mirrored changes in flow rate indicates that water in CPS-1 is not being diluted during increased flow events and the CPS-1 water is originating from a constant source such as the mine pool and not shallow flow paths.

Table XI: CPS-1 Calculated Loads

Location	Date Sampled	Flow Rate (L/min)	As (mg/min)	Ca (mg/min)	Cd (mg/min)	Co (mg/min)	Cu (mg/min)	Fe (mg/min))	Mg (mg/min)	Mn (mg/min)	Zn (mg/min)
CPS-1	8/16/14	8.23	0.058	314	1.09	0.247	93.5	0.115	174	27.8	82.4
CPS-1	8/30/14	11.7	0.012	428	1.45	0.340	128	0.152	238	37.8	112
CPS-1	9/20/14	7.52	B.D.	292	1.01	0.241	86.2	0.135	164	25.9	76.2
CPS-1	10/14/14	5.02	B.D.	217	0.74	0.176	62.6	0.090	121	19.2	55.4
CPS-1	10/24/14	5.95	0.024	271	0.93	0.202	77.4	0.273	151	23.8	69.0

B.D. indicates below detection limits

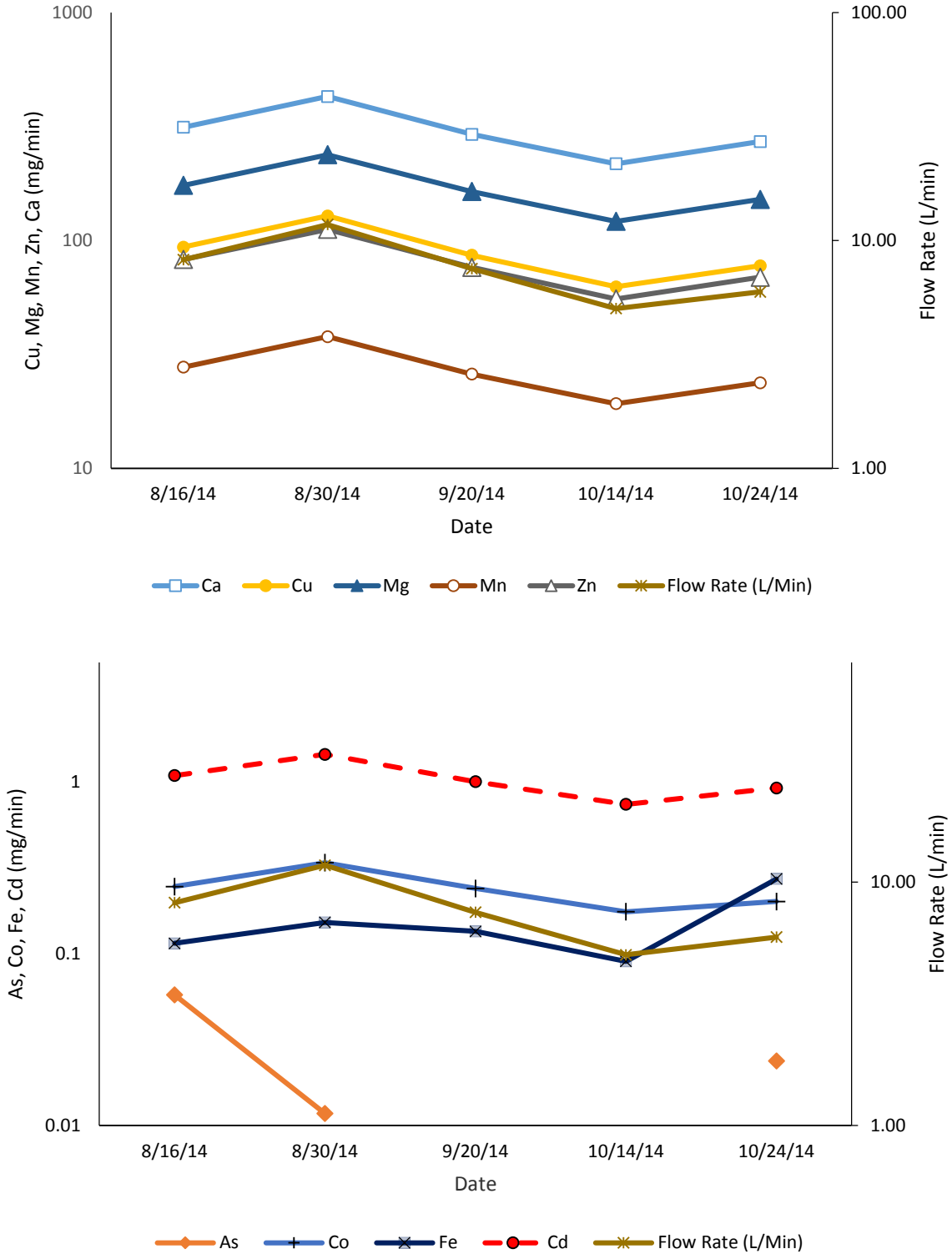

Figure 19: CPS-1 Calculated Loads for Selected Analytes

4.2. Water Isotopes

As discussed by Ghomshei & Allen (2000) stable water isotopes can be used to identify the origins of springs. Seasonal changes in the δ^2H and $\delta^{18}O$ composition of precipitation and surface water is the result of Rayleigh distillation caused by either rainout or evaporation (Clark and Fritz, 1997). The isotopic composition of small streams and shallow groundwater can change with the seasons in response to seasonal changes in $\delta^{18}O$ and δ^2H of rain and snow. However, a large volume of water in a mine pool has a much larger residence time, so that seasonal changes in recharge waters are averaged out (Walton-Day & Poeter, 2009). The isotopic composition of δ^2H and $\delta^{18}O$ of the groundwater seeps, mine pool, and wells at the Combination Mine plotted close to the Butte MWL or the Butte LEL (from Gammons et al., 2006). CPS-1 samples showed little seasonal change throughout the study and plotted close to the Butte MWL and mine pool samples (Figure 14). The lack of seasonal changes from the samples collected at CPS-1 indicates that the water forming CPS-1 is from a large reservoir.

CPS-2 and CPS-8 plotted closer to the Butte LEL and also were heavier than the mine pool samples. Both CPS-2 and CPS-8 showed variations throughout the study period (Figure 12 and Figure 13). During the study period CPS-2 and CPS-8 had water present, however later in the season both seeps were not as large. The diminished size of the seeps could cause the samples to plot with a stronger evaporated signature as water evaporated from the slow-moving spring, however samples collected towards the end of the study period were lighter than some samples collected earlier. Since the composition of δ^2H and $\delta^{18}O$ of CPS-2 and CPS-8 still changed throughout the study beyond just evaporation enrichment of the seeps it indicates that there is seasonal changes of the stable water isotopes to the source of the seeps. The seasonal changes and heavier isotopes for CPS-2 and CPS-8 are indicative of local recharge and a short-

residence time, as opposed to a large reservoir and long residence time for the mine pool and CPS-1.

4.3. Sulfate Isotopes

As discussed by Seal (2003) and Balci et al. (2007), the O-isotopic composition of dissolved sulfate can be used to infer the physico-chemical conditions during oxidation of primary sulfide minerals. For example, in many acid mine drainage settings, oxidation of pyrite by dissolved Fe^{3+} (ferric iron) takes place in the absence of molecular O_2, and can be written as follows:

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (1)$$

In reaction (1), all of the O in the sulfate that is produced comes from the water molecule, and therefore δ^{18}O-sulfate will be the same as δ^{18}O-water. In the opposite extreme, the oxidation of pyrite by molecular O_2 can be written as follows:

$$FeS_2(s) + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (2)$$

In reaction 2, only 1/8 of the O in the sulfate comes from water, with the remainder coming from the O_2 molecule. Because atmospheric O_2 is very heavy ($\delta^{18}O = +23.5$, Kroopnik and Craig, 1972), incorporation of oxygen from O_2 into the sulfate molecule will raise the value of δ^{18}O-sulfate. As discussed by Seal (2003), dissolved sulfate in acid mine drainage settings is usually formed by a mixture of reactions (1) and (2).

In Figure 20, the O-isotope compositions of dissolved sulfate from Black Pine are plotted vs. δ^{18}O-water for the same samples. The dashed lines show the relative contributions of oxygen from H_2O vs. O_2 that have wound up in the dissolved sulfate. Most of the Black Pine samples have isotopic compositions consistent with 85 to 90% of the oxygen in sulfate having come from water, and 10-15% from atmospheric O_2. The CPSW, CMMW-2, and North Area Spring

samples have heavier values of δ^{18}O-SO_4, indicating a greater percentage (~ 30%) of O in SO_4 coming from atmospheric O_2.

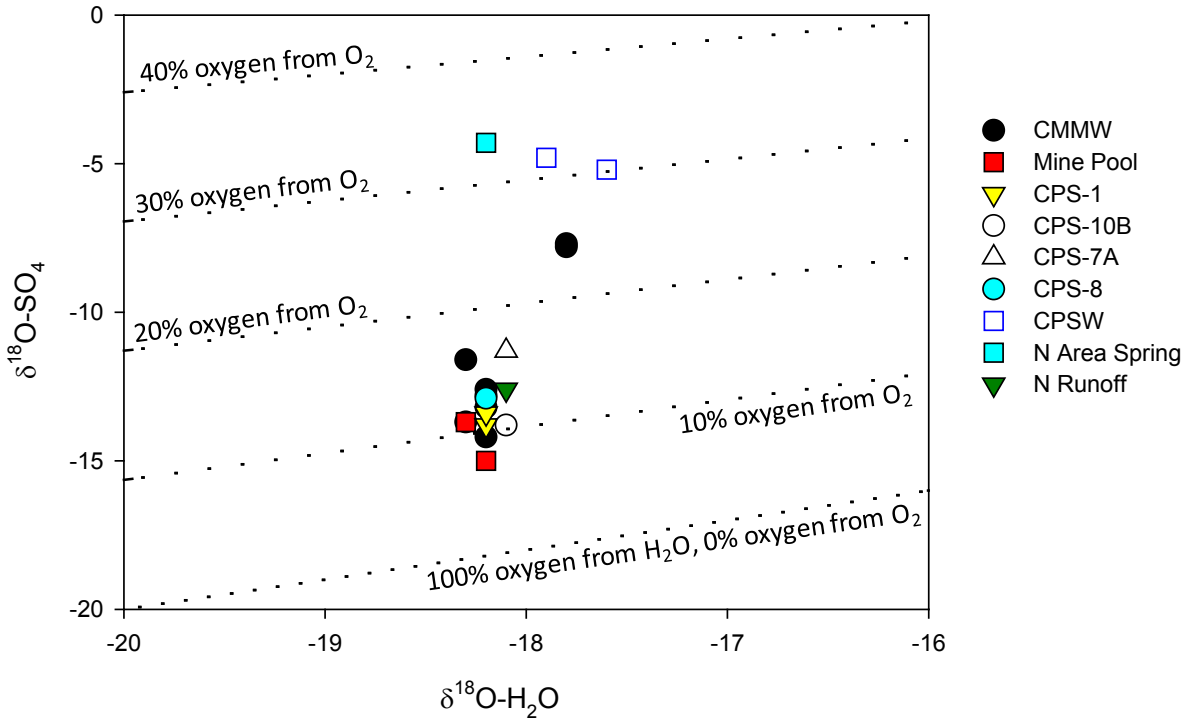

Figure 20: Plot of δ^{18}O-sulfate vs. δ^{18}O-water. See text for explanation of the dashed lines.

The S-isotopic composition of dissolved sulfate varies little during the oxidation of pyrite or other sulfide minerals and should resemble the S-isotopic composition of the sulfide mineral (Seal, 2003; Balci et al., 2007). Analysis of the δ^{34}S of sulfate during this study shows the majority of samples are in a narrow range of +4.5 to +5.5 ‰. CMMW-8 was consistently lighter in δ^{34}S, while CMMW-2, CPS-7A, and North Area Spring where consistently heavier. CPS-1, mine pool, and laboratory leachate samples were in the range of +4.5 to +5.5 ‰. The source of δ^{34}S of sulfate for the samples in the narrow range is most likely from oxidation of sulfide minerals at the mine site. When mine water becomes exposed to anoxic conditions and bacterial

sulfate reduction occurs the $\delta^{34}S$ of the residual sulfate pool becomes heavier as isotopically light hydrogen sulfide is microbially produced (Seal, 2003). It is possible that the heavier samples (CMMW-2, CPS-7A, and North Area Spring) underwent bacterial sulfate reduction under anoxic conditions. Another exception to S-isotopic composition of dissolved sulfate not varying during oxidation of sulfide minerals is in some experimental studies when aqueous sulfide is oxidized under neutral or alkaline conditions the resulting $\delta^{34}S$ of sulfate is lighter than the parent sulfide (Seal, 2003). CMMW-8 is acidic however if the aqueous sulfide was oxidized under neutral conditions before it reached CMMW-8 it could result in the $\delta^{34}S$ of sulfate being lighter than the other samples.

4.4. Conceptual Model

Based on the findings of this study, the following is the author's conceptual model for the hydrogeochemistry of the Combination Mine area. At the present time, mine pool water, as well as background groundwater, flows downgradient to the east, towards the Combination waste rock pile. Some of this water with a shallower flow path interacts with the bottom of the pile, with severe water quality degradation due to leaching of solutes from the weathered waste rock. The existence of a buried French drain prevents this water from subbing to the surface, and directs it towards CPS-1. However, the water that reports to CPS-1 is probably a mixture of this degraded water and deeper water that never interacted with the waste pile. This explains the fact that the geochemistry of CPS-1 water is intermediate between that of the mine pool and the waste-rock leachate as determined in the benchtop experiment. Based on the lack of any seasonal variation in water isotope signature at CPS-1, it is concluded that most of the water at this station comes from the large and isotopically-mixed mine pool and not from shallow groundwater recharged from individual precipitation events.

5. Conclusions and Recommendations

The focus of this thesis was to determine if the groundwater seeps located at the Combination Mine are recharged by the flooded mine pool, shallow flow paths through the waste rock pile, or a combination of both. Analysis of stable water isotopes (δ^2H, $\delta^{18}O$), $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate and tracking temporal changes in geochemistry were all used in this study to identify the recharge source for groundwater seeps at the Combination Mine. This study primarily focused on three groundwater seeps and seepage collection point (CPS-1, CPS-2, and CPS-8) as these three seeps and seepage collection point were present for length of the study. The main conclusions are listed below:

- CPS-1 has higher concentrations of analytes than the mine pool. Changes in the loads at CPS-1 mirror changes in discharge. Stable water isotopes for CPS-1 indicate the source of CPS-1 recharge is a large reservoir such as the mine pool and not shallow flow paths through the waste rock pile.
- The S- and O-isotopic composition of sulfate at CPS-1 is similar to the isotopic composition of sulfate in the mine pool.
- Benchtop experiments in which lab water was interacted with samples of mine waste from the Combination waste rock dump showed severe degradation in pH and metal and sulfate concentrations. The sulfate that leached out of the experiments had the same isotopic composition as the sulfate at CPS-1.
- Since the mine pool water degrades through interaction with the dump on its way to CPS-1, removal of the dump should improve the quality of any water that continues to seep to the surface in this area.

- CPS-2 concentrations of analytes were typically lower than the mine pool. There was little temporal changes in concentrations at CPS-2 and CPS-8. Stable water isotopes from CPS-2 and CPS-8 plotted heavier and closer to the local evaporation line than the mine pool sample and varied throughout the study. The source of CPS-2 and CPS-8 is most likely not directly impacted by the mine pool water.

Recommendations for further investigations include the following:

- Collect samples of mine pool water at greater depth, to see if the chemistry is stratified.
- Continue collecting samples of groundwater and seeps after the waste rock pile is removed to see if water quality of the seeps and shallow groundwater improves.

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Appendix A: Laboratory Data

Table A1:ICP-OES Analysis Results. All data in mg/L and adjusted for dilution.

Sample ID	Date	As	Be	Ca	Cd	Co	Cr	Cu	Fe	Li	Mg	Mg	Mn	Mo	Ni
CPS-1	8/16/2014	0.007	0.004	38.11	0.133	0.03	0.02	11.36	0.014	0.01	22.29	21.2	3.378	B.D.	B.D.
CPS-1	8/30/2014	0.001	0.004	36.48	0.124	0.029	0.02	10.92	0.013	0.009	21.38	20.26	3.223	B.D.	B.D.
CPS-1	9/20/2014	B.D.	0.004	38.86	0.134	0.032	0.01	11.46	0.018	0.011	22.81	21.79	3.448	B.D.	B.D.
CPS-1	10/14/2014	B.D.	0.005	43.15	0.148	0.035	0.02	12.46	0.018	0.011	25.27	24.13	3.824	B.D.	B.D.
CPS-1	10/24/2014	0.004	0.005	45.66	0.156	0.034	0.02	13.02	0.046	0.011	26.76	25.48	3.996	B.D.	B.D.
CPS-2	8/16/2014	0.007	B.D.	5.136	B.D.	0.005	0.02	B.D.	0.098	B.D.	2.042	1.859	0.028	B.D.	B.D.
CPS-2	8/30/2014	B.D.	0.001	3.944	B.D.	0.006	0.02	B.D.	0.329	B.D.	1.625	1.506	0.031	B.D.	B.D.
CPS-2	9/20/2014	B.D.	0.001	4.688	B.D.	0.004	0.01	B.D.	0.127	B.D.	1.981	1.744	0.021	B.D.	B.D.
CPS-2	10/14/2014	B.D.	0.001	4.375	B.D.	0.004	0.02	B.D.	0.072	B.D.	1.865	1.624	0.009	B.D.	B.D.
CPS-8	8/16/2014	B.D.	0.001	6.737	B.D.	0.003	0.01	B.D.	0.04	0.001	3.535	3.147	0.018	B.D.	B.D.
CPS-8 DUP	8/16/2014	B.D.	0.001	6.822	B.D.	0.005	0.02	B.D.	0.038	0.001	3.595	3.186	0.016	0.001	B.D.
CPS-8	8/30/2014	B.D.	0.001	8.157	B.D.	0.003	0.02	B.D.	0.056	0.002	4.216	3.74	0.031	B.D.	B.D.
CPS-8	9/20/2014	B.D.	0.001	7.408	B.D.	0.003	0.01	B.D.	0.034	0.002	3.893	3.417	0.023	B.D.	B.D.
CPS-8	10/14/2014	B.D.	0.001	7.278	B.D.	0.003	0.02	B.D.	0.044	0.001	3.824	3.322	0.021	0.001	B.D.
CPS-8	10/24/2014	B.D.	0.001	7.661	B.D.	0.003	0.02	B.D.	0.211	0.001	4.076	3.458	0.073	0.001	B.D.
CMMW-1	10/24/2014	B.D.	0.001	5.933	B.D.	0.005	0.02	B.D.	0.003	0.003	4.823	4.071	0.001	B.D.	B.D.
CMMW-2	10/24/2014	0.062	0.001	176.3	0.008	0.007	0.02	0.376	0.33	0.005	50.29	44	0.156	B.D.	B.D.
CMMW-3	10/24/2014	B.D.	0.002	59.59	0.045	0.016	0.02	1.636	0.49	0.017	31.65	27.05	1.314	B.D.	B.D.
CMMW-6	10/24/2014	B.D.	0.001	12.36	B.D.	0.007	0.02	B.D.	0.069	0.001	6.941	5.869	0.477	B.D.	B.D.
CMMW-8	10/24/2014	B.D.	0.002	114.5	0.098	0.009	0.02	2.026	0.015	0.043	87.52	73.73	2.053	B.D.	B.D.
CMMW-8 DUP	10/24/2014	B.D.	0.002	114.5	0.098	0.008	0.02	2.025	B.D.	0.042	88.3	73.96	2.045	B.D.	B.D.
MINE POOL	10/24/2014	B.D.	0.001	26.77	0.061	0.012	0.02	3.416	0.077	0.004	11.66	9.753	1.413	B.D.	B.D.
MINE POOL DUP	10/24/2014	B.D.	0.001	27.29	0.063	0.011	0.02	3.463	0.083	0.006	11.85	9.921	1.428	B.D.	B.D.
Waste Rock 1		B.D.	0.024	480.1	0.719	0.3	0.02	68.38	0.141	0.089	113.5	95.98	49.02	B.D.	B.D.
Waste Rock 2		0.307	0.115	422.6	3.27	0.618	0.22	488.7	123.4	0.174	250.2	204.6	103.8	0.001	0.331
Waste Rock 3		0.022	0.053	433.4	1.495	0.36	0.04	450.4	1.567	0.113	144.6	122.2	127.2	0.01	0.041
Waste Rock 3 DUP		0.013	0.052	439.8	2.243	0.548	0.03	447.1	1.575	0.112	144.9	122.3	127.7	0.007	0.213

B.D. – Below detection limits

Dup–Duplicate sample

(cont.) **Table A1:ICP-OES Analysis Results. All data in mg/L and adjusted for dilution**

Sample ID	*Date*	*Pb*	*Sb*	*Se*	*Sr*	*Ti*	*Tl*	*V*	*Zn*
CPS-1	8/16/2014	B.D.	B.D.	B.D.	0.209	0.002	0.04	B.D.	10.02
CPS-1	8/30/2014	0.016	B.D.	B.D.	0.201	0.003	0.03	B.D.	9.533
CPS-1	9/20/2014	0.01	B.D.	B.D.	0.212	0.002	0.03	B.D.	10.13
CPS-1	10/14/2014	0.016	B.D.	B.D.	0.232	0.002	0.03	B.D.	11.02
CPS-1	10/24/2014	0.016	B.D.	B.D.	0.244	0.002	0.03	B.D.	11.6
CPS-2	8/16/2014	B.D.	B.D.	B.D.	0.037	0.001	0.02	B.D.	0.002
CPS-2	8/30/2014	0.007	B.D.	B.D.	0.033	0.001	0.02	B.D.	0.003
CPS-2	9/20/2014	0.015	B.D.	B.D.	0.039	0.001	0.02	B.D.	0.005
CPS-2	10/14/2014	0.01	B.D.	B.D.	0.036	0.003	0.03	B.D.	0.005
CPS-8	8/16/2014	0.014	B.D.	B.D.	0.049	0.004	B.D.	B.D.	0.112
CPS-8 DUP	8/16/2014	0.018	B.D.	B.D.	0.05	0.003	0.04	B.D.	0.114
CPS-8	8/30/2014	0.015	B.D.	B.D.	0.06	0.003	B.D.	B.D.	0.129
CPS-8	9/20/2014	0.007	B.D.	B.D.	0.053	0.001	0.02	B.D.	0.148
CPS-8	10/14/2014	B.D.	B.D.	B.D.	0.052	0.003	0.04	B.D.	0.172
CPS-8	10/24/2014	B.D.	B.D.	B.D.	0.055	0.002	0.02	B.D.	0.113
CMMW-1	10/24/2014	0.012	B.D.	B.D.	0.058	B.D.	0.02	B.D.	0.001
CMMW-2	10/24/2014	0.032	0.059	B.D.	0.579	0.011	0.01	B.D.	1.157
CMMW-3	10/24/2014	0.016	B.D.	0.005	0.332	0.004	0.01	B.D.	3.81
CMMW-6	10/24/2014	0.005	B.D.	0.004	0.097	0.001	B.D.	B.D.	0.031
CMMW-8	10/24/2014	0.018	0.002	0.002	0.624	0.004	0.02	B.D.	6.437
CMMW-8 DUP	10/24/2014	0.025	B.D.	0.006	0.628	0.003	0.01	B.D.	6.392
MINE POOL	10/24/2014	0.04	0.06	0.002	0.095	0.001	0.04	B.D.	3.848
MINE POOL DUP	10/24/2014	0.032	0.056	B.D.	0.097	0.003	0.02	B.D.	3.913
Waste Rock 1		0.084	0.044	0.033	1.127	0.01	B.D.	B.D.	67.58
Waste Rock 2		0.152	0.125	0.026	0.72	0.033	B.D.	B.D.	237.6
Waste Rock 3		0.362	0.126	0.06	0.825	0.029	B.D.	B.D.	121.9
Waste Rock 3 DUP		0.571	0.18	0.068	0.821	0.03	B.D.	B.D.	184.2

B.D. – Below detection limits
Dup–Duplicate sample

Table A2: $\delta^{34}S$ and $\delta^{18}O$ of Sulfate Analysis Results.

Location	*Date*	*$\delta^{34}S$ (‰)*	*$\delta^{18}O$ (‰)*	*sulfate (mg/L)*
CMMW-1	5/8/2014	insufficient sample volume		2.2
	10/24/2014	insufficient sample volume		7
CMMW-2	5/8/2014	6.9	-7.7	181
	10/24/2014	7.3	-7.8	860
CMMW-3	5/8/2014	5.2	-14.2	476
	10/24/2014	4.8	-12.6	340
CMMW-4	5/8/2014	5.3	-13.7	268
	10/24/2014	5	-11.6	180
CMMW-5	5/8/2014	5.2	-15	108
	10/24/2014	Well Dry		
CMMW-6	5/8/2014	insufficient sample volume		6.6
	10/24/2014	insufficient sample volume		26
CMMW-7	5/8/2014	5.1	-14.7	503
	10/24/2014	Well Dry		
CMMW-8	5/8/2014	3.2	-13.2	614
	10/24/2014	2.9	-12.8	740
CPS-1	5/8/2014	5.3	-13.8	333
	10/24/2014	5.2	-13.4	320
CPS-2	5/9/2014	insufficient sample volume		4.3
	10/24/2014	Seep Dry		
CPS-10B	5/21/2014	5.2	-13.8	251
	10/24/2014	Seep Dry		
CPS-7A	5/9/2014	6.5	-11.3	76
	10/24/2014	Seep Dry		
CPS-8	5/21/2014	5.3	-12.9	33.8
	10/24/2014	insufficient sample volume		20
CPSW-1	5/9/2014	5.4	-4.8	17.9
CPSW-2	5/9/2014	5	-5.2	22.4
DTRD	5/8/2014	5.4	-13.5	193
	10/24/2014	Seep Dry		
Mine Pool	5/9/2014	4.9	-15	24.3
	10/24/2014	4.9	-13.7	90
Mine Pool dup	5/9/2014	5	-14.6	24.3
N Area Spring N	5/9/2014	7.4	-4.3	24.4
	10/24/2014	Seep Dry		
N Runoff	5/9/2014	5.3	-12.6	53.9
	10/24/2014	Seep Dry		
Wet Vault	5/8/2014	5.3	-13.8	259
Waste Rock 1		5.3	-13.4	700

(cont.) **Table A2: $\delta^{34}S$ and $\delta^{18}O$ of Sulfate Analysis Results.**

Location	*Date*	*$\delta^{34}S$ (‰)*	*$\delta^{18}O$ (‰)*	*sulfate (mg/L)*
Waste Rock 2	—— ——	5.2	-12.1	5500
Waste Rock 2 dup	—— ——	5.2	-12.2	5500
Waste Rock 3	—— ——	5.0	-14.4	3000

Appendix B: Sample Log and Field Notes

Date	Time	Depth to Water	Discharge (gpm)	DO (mg/L)	pH	Temp (°C)	Eh (mV)	Sc (us/cm)	Samples collected	Notes
					CMMW-6					
5/8/2014	12:15	36.07	--	16.85	7.82	6.04		54	Sulfate Isotope	
10/24/2014	15:01	52.01	--	5.58	6.37	8.68	371	1537	Sulfate Isotope, Water Isotope ICP-OES	
					CMMW-8					
5/8/2014	14:45	43.62	--	24.66	5.25	7.43		712	Sulfate Isotope	
10/24/2014	14:11	59.52	--	7.7	5.9	7.75	459	1216	Sulfate Isotope, Water Isotope ICP-OES	
					CMMW-7					
5/8/2014	13:20	51.51	--	11.19	4.31	5.82	--	591	Sulfate Isotope	
					CMMW-5					
5/8/2014	12:25	58.06	--	9.81	5.21	6.59	--	150	Sulfate Isotope	
					CMMW-4					
5/8/2014	14:47	0	--	10.98	4.63	4.7	--	355	Sulfate Isotope	
10/24/2014	12:32	24.01	--	8.68	5.27	8.1	443	426.2	Sulfate Isotope, Water Isotope ICP-OES	
					CMMW-3					
5/8/2014	15:40	28.05	--	14.32	4.67	6.38		549	Sulfate Isotope	
10/24/2014	12:25	47.46	--	8.66	5.71	7.26	438	724.4	Sulfate Isotope, Water Isotope ICP-OES	
					CMMW-2					
5/8/2014	12:55	42.51	--	--	--	--	--	--	Sulfate Isotope	

Date	Time	Depth to Water	Discharge (gpm)	DO (mg/L)	pH	Temp (°C)	Eh (mV)	Sc (us/cm)	Samples collected	Notes
10/24/2014	15:24	44.74	--	2.73	6.01	7	--	--	Sulfate Isotope, Water Isotope ICP-OES	Water in well is below screening interval, not enough water for parameters
					CMMW-1					
5/8/2014	17:32	48.42	--	9.26	6.31	6.54	--	85	Sulfate Isotope	
10/24/2014	11:36	45.39	--	6.06	6.42	8.68	369	96.5	Sulfate Isotope, Water Isotope ICP-OES	
					DTRD					
5/8/2014	18:10	--	0.7	16.69	4.21	6.56	--	219	Sulfate Isotope, Water Isotope	
					CPS-1					
5/8/2014	18:33	--	18.8	12.43	4.42	6.02	--	412	Sulfate Isotope, Water Isotope	
7/19/2014	13:08	--	3.15	--	--	--	--	--	water Isotopes	
8/3/2014	14:15	--	2.73	--	--	--	--	--	water Isotopes	
8/16/2014	15:05	--	2.17	--	3.53	12.1	523	485	water Isotopes, ICP-OES	
8/30/14	15:30	--	3.10	--	3.8	9.54	508	479.5	water Isotopes, ICP-OES	
9/20/14	15:10	--	1.99	--	4.03	9.39	529	534.1	water Isotopes, ICP-OES	
10/14/14	18:16	--	1.33	--	3.83	10.01	494	617.1	water Isotopes, ICP-OES	
10/24/14	16:17	--	1.57	--	4.56	6.52	497	501.7	Sulfate Isotopes, water Isotopes, ICP-OES	

Date	Time	Depth to Water	Discharge (gpm)	DO (mg/L)	pH	Temp (°C)	Eh (mV)	Sc (us/cm)	Samples collected	Notes
					Wet Vault					
5/8/2014	18:39	--	--	12.08	5.17	5.54	--	313	Sulfate Isotope, Water Isotope	
					Mine Pool					
5/9/2014	8:45	--	--	16.74	7.38	3.56	--	--	Sulfate Isotope, Water Isotope	
5/9/2014	8:50	--	--	16.74	7.38	3.56	--	--	Sulfate Isotope, Water Isotope	Duplicate
10/24/2014	17:30	--	--	14.29	6.23	5.72	432	296.8	water Isotopes, Sulfate isotopes ICP-OES	
					CPSW-1					
5/9/2014	9:16	--	100	10.82	7.11	5.48	--	59	Sulfate Isotope, Water Isotope	
7/19/2014	--	--	--	--	--	--	--	--	--	Dry
					CPSW-2					
5/9/2014	9:40	--	150	11.62	7.12	5.31	--	48	Sulfate Isotope, Water Isotope	
7/19/2014	--	--	--	--	--	--	--	--	--	Dry, with few stagnant puddles
					CPS-2					
5/9/2014	9:49	--	4	10.57	6.32	4.89	--	33	Sulfate Isotope, Water Isotope	
7/19/2014	14:00	--	--	--	--	--	--	--	water Isotopes	Negligible flow
8/3/2014	14:37	--	--	--	--	--	--	--	water Isotopes	No apparent flow, stagnant puddle

Date	Time	Depth to Water	Discharge (gpm)	DO (mg/L)	pH	Temp (°C)	Eh (mV)	Sc (us/cm)	Samples collected	Notes
CPS-2										
8/16/2014	15:45	--	--	--	5.84	13.6	399	64	water Isotopes, ICP-OES	No apparent flow, most water in drainage since spring.
8/30/14	16:25	--	--	--	5.27	15	442	112	water Isotopes, ICP-OES	Negligible flow
9/20/14	15:52	--	--	--	6.03	15.61	376	60.2	water Isotopes, ICP-OES	
10/14/14	18:00	--	--	--	5.57	11.17	357	76.2	water Isotopes, ICP-OES	Minimal amount of water present
North Runoff										
5/9/2014	10:10	--	6.3	11.84	6.57	5.34	--	97	Sulfate Isotope, Water Isotope	
CPS-10b										
5/9/2014	10:28	--	0.8	9.51	4.23	5.49	--	340	Sulfate Isotope, Water Isotope	
5/21/2014	18:30	--	--	--	--	--	--	262	Sulfate Isotopes	Recollected sulfate sample
N. Area Springs N										
5/9/2014	10:40	--	4	11.57	5.88	5.04	--	64	Sulfate Isotope, Water Isotope	
CPS-7A										
5/9/2014	11:44	--	0.3	12.74	5.08	6.57	--	128	Sulfate Isotope, Water Isotope	

Date	Time	Depth to Water	Discharge (gpm)	DO (mg/L)	pH	Temp (°C)	Eh (mV)	Sc (us/cm)	Samples collected	Notes
CPS-8										
5/9/2014	12:07	--	0.5	12.97	6.22	7.9	--	85	Sulfate Isotope, Water Isotope	
5/21/2014	18:55	--	--	--	--	--	--	230	Sulfate Isotopes	Recollected sulfate sample
7/19/2014	14:29	--	--	--	--	--	--	--	Water Isotopes	No flow
8/3/2014	15:03	--	--	--	--	--	--	--	Water Isotopes, ICP-OES	No flow, water very turbid
8/16/2014	16:20	--	--	--	6.69	17	371	91.5	Water Isotopes, ICP-OES	No flow, water very turbid
8/30/14	17:05	--	--	--	6.15	14.5	372	106.9	Water Isotopes, ICP-OES	No flow, turbid water
9/20/2014	14:22	--	--	--	5.7	16.62	364	162.4	Water Isotopes, ICP-OES	
10/14/2014	18:47	--	--	--	5.53	10.03	316	156.8	Water Isotopes, ICP-OES	
10/24/2014	18:32	--	--	--	6.29	6.88	183	95.9	Sulfate Isotopes, water Isotopes, ICP-OES	
Waste Rock 1										
11/24/2014	13:20	--	--	--	3.52	--	--	2689	Sulfate Isotopes, ICP-OES	Leachate experiment
Waste Rock 2										
11/24/2014	13:20	--	--	--	2.48	--	--	4746	Sulfate Isotopes, ICP-OES	Leachate experiment
Waste Rock 3										
11/24/2014	13:20	--	--	--	3.02	--	--	3883	Sulfate Isotopes, ICP-OES	Leachate experiment

Appendix C: Photographs

C1. Seepage collection and pump back system, CPS-1 sample location access is through the man hole in the foreground.

C2. CPS-2 sample location (photo curtesy of Herrera Environmental Consultants).

C3. CPS-8 sample site location.

C4. Combination Mine adit

C5. Combination Mine waste rock pile.

SIGNATURE PAGE

This is to certify that the thesis prepared by Corey Swisher entitled "Hydrologic and Chemical Interaction Between Waste Dumps and a Flooded Mine Pool at the Combination Mine, Philipsburg District, Montana" has been examined and approved for acceptance by the Department of Geological Engineering, Montana Tech of The University of Montana, on this 28th day of April, 2017.

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